NEARSHORE WATER QUALITY AT THUNDER BAY, LAKE SUPERIOR, 1983

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by

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FOREWORD

The Ministry's investigation of water quality conditions in the Thunder Bay Area of Concern formed part of Ontario's contribution to the Lake Superior Intensive Surveillance and Monitoring Program of 1983. An earlier draft of this report was submitted to the International Joint Commission's Surveillance Work Group (September 1985) for inclusion in the international Lake Superior Task Force Report currently under preparation.

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ACKNOWLEDGEMENTS

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The author acknowledges the efforts of field personnel in the collection of samples and the efforts of the Water Quality, Microbiology, Inorganic Trace Contaminants and Pesticides Laboratory Sections in the analysis of these samples.

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SUMMARY

In the Canada/US Great Lakes Water Quality Board Annual Report of 1983 Thunder Bay was identified as one of the five Areas of Concern in Lake Superior (GLWQB, 1983). Specific reference was made to high levels of contamination in the lower Kaministikwia River, its outlets and the inner harbour. Contamination was attributed to industrial and municipal wastewater discharges from the City of Thunder Bay. This paper reports on water quality data collected in the Thunder Bay nearshore in the summer of 1983, contaminants in sediments collected in 1979 and young-of-the-year and sport fish collections of 1983. The 1983 data collections formed part of the Ministry of Environment's contributions to the 1983 Lake Superior International Study Year co-ordinated by the Water Quality Board's Surveillance Work Group.

The 1983 water quality results showed decreases from previous years in phosphorus, phenols, iron and copper levels. Comparisons, however, remain subjective due to changes in survey design, sampling locations and analytical methods.

In 1983, inshore surface waters in Thunder Bay contained the highest levels of contaminants (bacteria, trace organics, inorganics) and nutrients with a zone of most degraded water quality radiating from the Kaministikwia River delta. Water quality objectives were occasionally exceeded for PCB's, iron, aluminum, cadmium and copper. This zone of influence extended as far east as the Welcome Islands (7.5 km) and south to Pie Island (13 km). Also, the presence of chlorophenols and other trace organic compounds extending northeast from Grand Point and including the Welcome Islands, suggests Great Lakes Forest Products Ltd. or the Abitibi-Price Pulp and Paper Mills as the possible sources. Further investigations are required to identify the specific sources of these chemicals.

Mercury levels in the Thunder Bay area sediments have shown a dramatic decrease from 1971 to 1979 due to the closing of Dow Chemical's chlor-alkali plant on the Kaministikwia River in 1974. PCB levels in young-of-the-year spottail shiners collected in the Kaministikwia and Mission Rivers in 1983 were significantly greater than in the 1979 collections, while levels of organochlorine compounds have generally decreased. Ongoing investigations will determine if these changes signify a trend.

CONCLUSIONS AND RECOMMENDATIONS

1. The presence of trace organic compounds and chlorophenols in the area extending northeast from Grand Point and including the Welcome Islands requires further investigation into specific sources of these substances. Thunder Bay's pulp and paper mills are the most likely contributors, however, atmospheric contributions and resuspension of sediments at former dredge spoils dumping sites may also be possible sources. Effluent sampling and characterization at the 4 pulp and paper mills in conjunction with ambient water sampling will assist in identifying specific inputs both in terms of quantity and quality.

2. Further knowledge of the significance and fate of resin acids in the aquatic environment is required to allow quantitative assessments to be made. The presence/absence of these substances in Thunder Bay has now been documented, further assessments should be undertaken to address the issues of: the impact on aquatic life; water use impairment; and long-term environmental degradation.

3. Inshore surface waters in Thunder Bay contain the highest bacterial inorganic and organic contaminant levels. Further surveys should be designed to gain more information on the mixing of the Kaministikwia River waters and lake waters and on the vertical gradation further from shore thereby providing a link between sources and the environmental fate of contaminants.

4. Characterizing the spatial and temporal patterns in Thunder Bay water quality provides valuable information for determining the optimum survey design for future studies. The spatial pattern suggests a zone of most degraded water quality in an area close to shore and radiating out from the Kaministikwia River delta. This zone of influence extends as far east as the Welcome Islands. Conditions approach background levels past the Welcome Islands in the east and in the south towards Pie Island and the open lake.

Because of the daily variability encountered in the 1983 water quality results based on a 3-day sampling regime, it is concluded that this approach has been inadequate for an area as complex as Thunder Bay. Sample replication and a greater frequency of collections would provide more insight into the determination of "average" conditions as well as extreme conditions. In addition, effluent characterization and variability studies are necessary to assist in the identification of specific sources and the implementation of remedial measures by dischargers with respect to quality and quantity of contaminants in their effluent.

5. Some decreases from previous years in phosphorus levels, phenols, iron and copper were observed in the 1983 water quality results. However, comparisons with previous year's data remain subjective due to changes in survey design, sampling locations and analytical methods.

6. Mercury levels in the Thunder Bay area sediments have shown a dramatic decrease from 1971 to 1979. The maximum levels observed in both years were from sediments in the northern end of the inner harbour.

7. PCB levels in young-of-the-year spottail shiners collected in the Kaministikwia and Mission Rivers in 1983 were significantly greater than in the 1979 collections while levels of organochlorine compounds have generally decreased. Investigations should be continued to determine if these changes signify a trend.

INTRODUCTION

Investigations of water quality, sediment quality and the benthic community of the Thunder Bay area over the past two decades have identified water pollution problems which are a direct result of the industrialization and urbanization that has taken place (Figures 1, 2 & 2a). Although Lake Superior's open waters still remain largely unaffected by man's influence, it is important to preserve the existing high water quality in the face of further population and industrial growth and to protect the quality of its water for a variety of local uses. In particular, the nearshore, being the site of the greatest water use is also therefore, the area of primary concern.

In October, 1965, the Ontario Water Resources Commission (OWRC) conducted a biological survey in the Kaministikwia River and Thunder Bay to investigate fish tainting and the declining success of commercial fisheries. The absence or unbalanced nature of bottom faunal communities was reported and attributed to organic enrichment from domestic wastes, wood fibre discharged from pulp and paper mills and starch wastes from industrial and municipal sources (OWRC, 1967). The study concluded that Thunder Bay harbour water quality was moderately to heavily impaired.

In 1970, a survey by the Ontario Ministry of the Environment (MOE, 1972) found that the surface waters in the lower Kaministikwia River basin and Thunder Bay's inner harbour (formed by a 5 mile breakwall) were being contaminated by local industrial and municipal wastewater discharges. The industrial sources accounted for approximately ninety percent of the oxygen consuming waste (BOD_5) inputs to the study area. Although the BOD_5 loadings from municipal sources were much lower, these contributed significantly to bacterial contamination and the input of nutrients. The findings also revealed: excessive loadings of suspended solids; an accumulation of organic materials and metals, including mercury in bottom deposits; aesthetic impairment; and the presence of potentially toxic and tainting substances. Although pollution abatement programs were underway, dissolved oxygen levels in the Kaministikwia River (Figure 2) during low flow periods remained insufficient to provide adequate protection for fish and other biota.

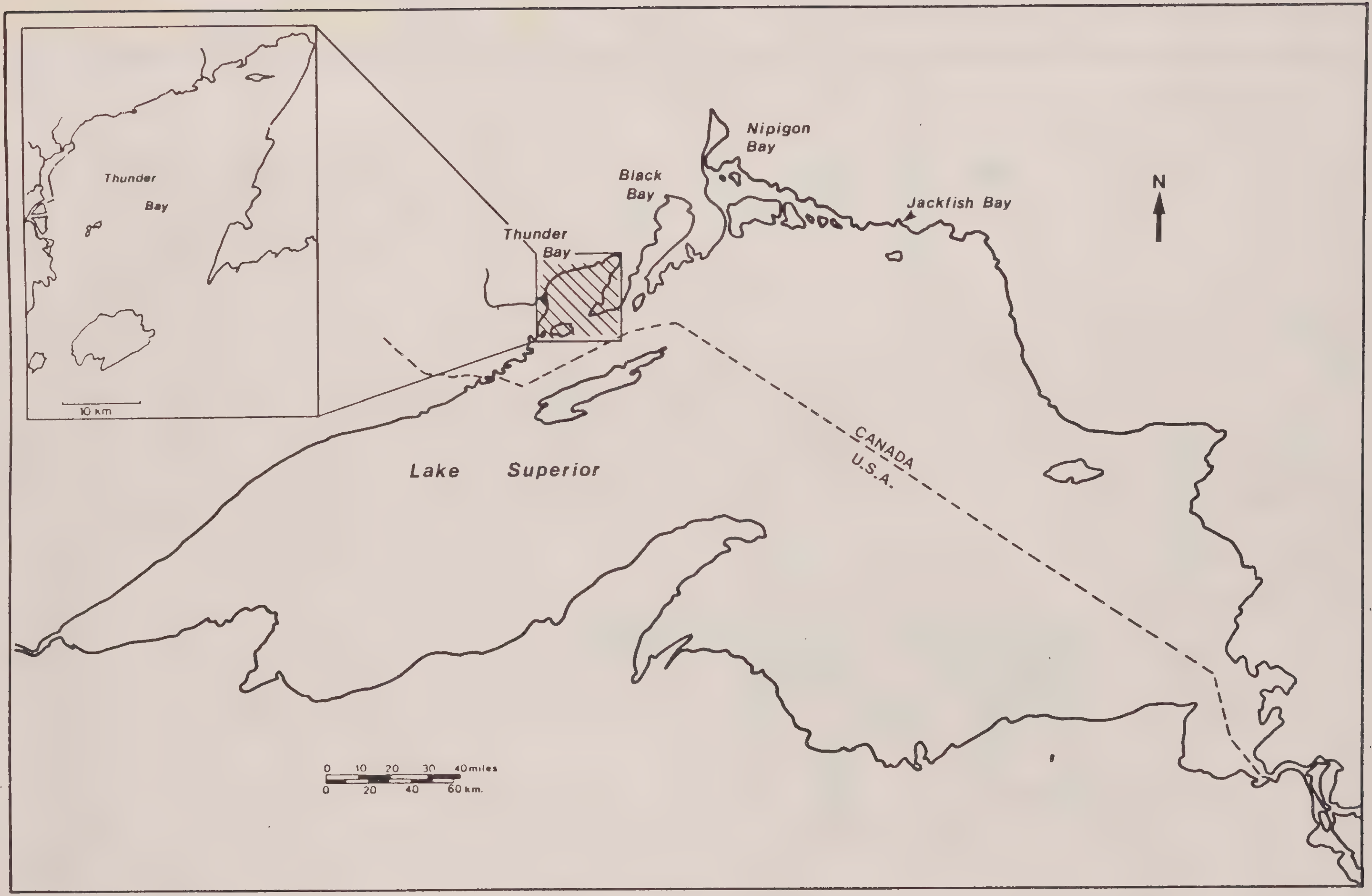


FIGURE 1: STUDY AREA

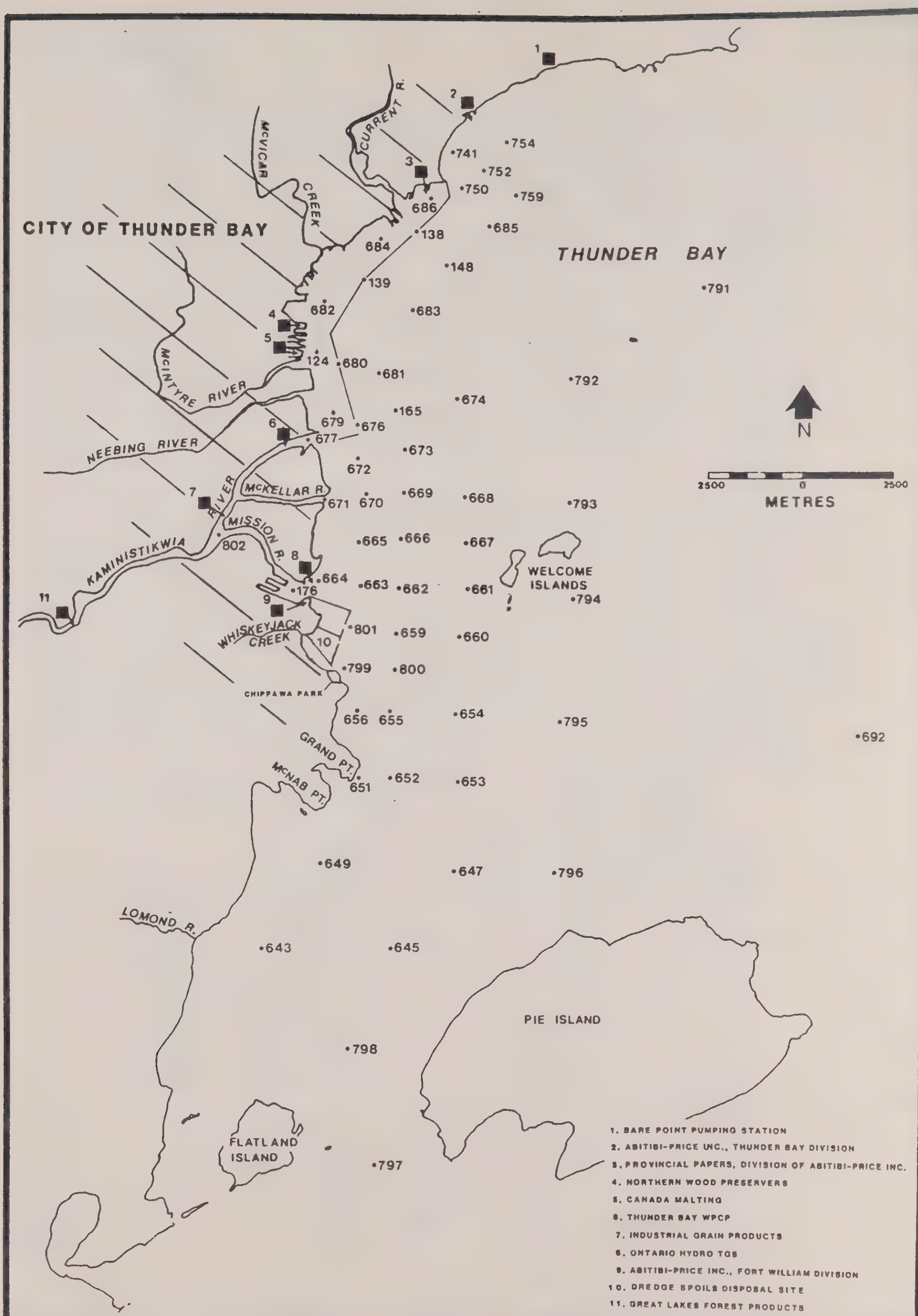


FIGURE 2 : STATION LOCATIONS

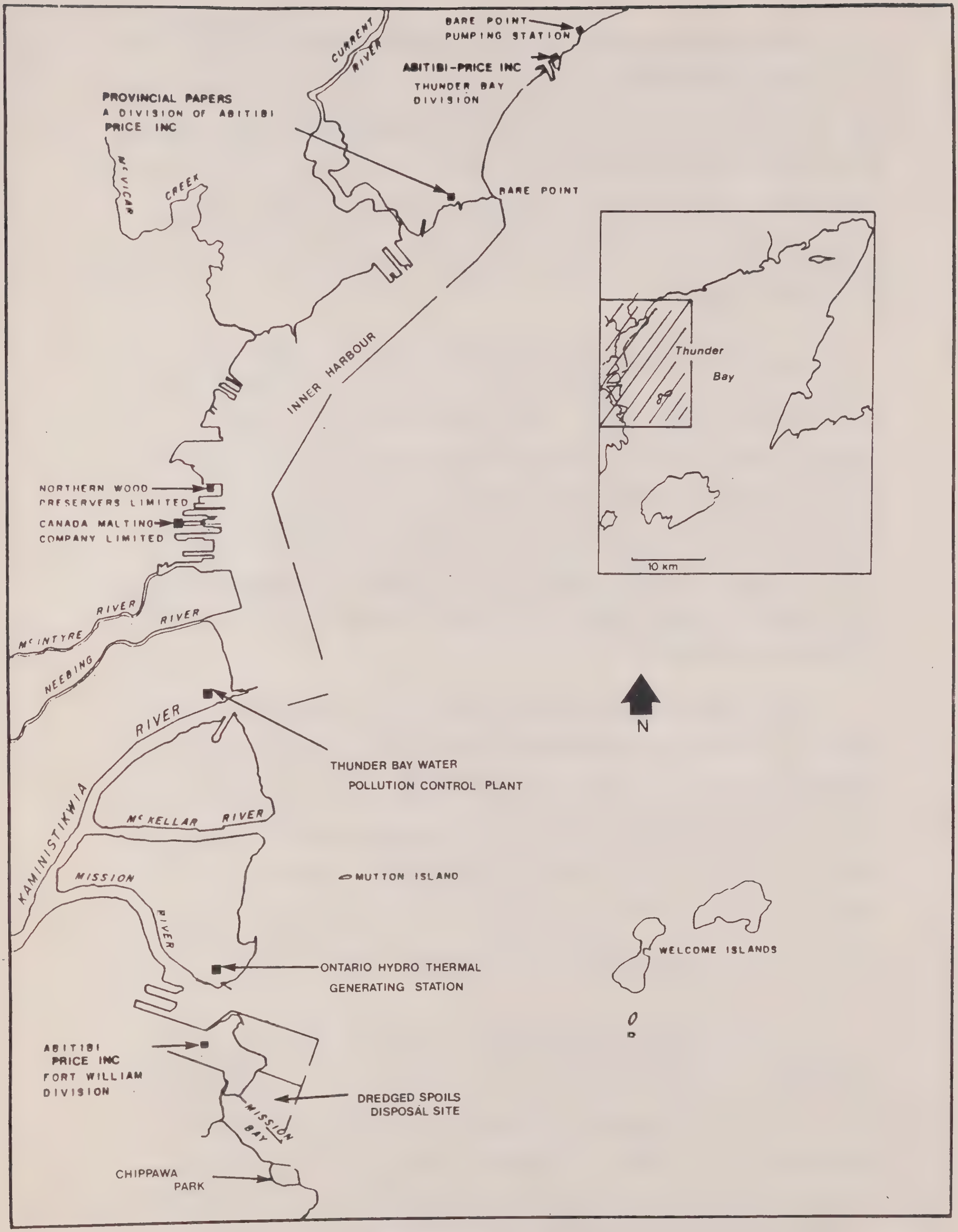


FIGURE 2a: THUNDER BAY'S INDUSTRIAL & MUNICIPAL DISCHARGES

In the Canada-U.S. Great Lakes Water Quality Board annual report of July 1976, Thunder Bay was identified as one of the five major problem areas in Lake Superior (GLWQB, 1976). Specific reference was made to high levels of contamination in the lower Kaministikwia River, its three outlets, the Kaministikwia, Mission and McKellar Rivers and Thunder Bay's inner harbour. (Figure 2) Depressed dissolved oxygen levels, bacterial contamination, nutrient and organic enrichment and elevated mercury levels in lake trout were identified as the concerns in the Thunder Bay area.

Substantial reductions in the biochemical oxygen demand (BOD) in the lower Kaministikwia River have taken place since the problem was first identified (MOE, 1972). These reductions resulted from: improved treatment of Great Lakes Forest Products effluent discharged to the river (e.g. a substantial removal of solids using clarifiers and sludge dewatering facilities resulted in lower bottom deposits and dredging activities; and biodegradation resulted in further reduction of the biochemical oxygen demand). Recirculation of wastewater streams from Industrial Grain Products on the Kaministikwia River also reduced BOD loadings substantially.

Remedial measures have improved the quality of industrial and municipal discharges as evidenced by ambient water quality surveys. Whereas water quality studies in the past have centred on phosphorus enrichment and bacterial contamination, recent investigations have emphasized trace organic and inorganic contaminants which require more sophisticated sampling and analytical techniques. Laboratory capabilities have improved, identifying previously undetected contaminants in water, sediment and the biota and providing a link between sources and the receiving environment.

This report interprets the water quality data collected in the Thunder Bay area in the summer of 1983 as part of the international Lake Superior intensive year study. This study was undertaken by the Ministry of the Environment to determine the degree and extent of impairment of the aquatic environment in the Thunder Bay area as a result of wastewater discharges from industrial and municipal sources. Analyses included chlorophenols, resin, aromatic and fatty acids,

metals and trace organics characteristic of pulp and paper mill discharges. Previous MOE studies of water and sediment quality and fish contaminant levels in the Thunder Bay region were assessed to supplement these findings and provide temporal comparisons.

WATER USE

The city of Thunder Bay is the largest Canadian city on Lake Superior. As a major port and the western terminus of the St. Lawrence Seaway, the main portion of Thunder Bay's economic base is from industry relating directly or indirectly to the activities of this port. Paper and wood products, as well as wheat and grain products, iron ore, bulk cargo, oil and coal are the major commodities handled.

The predominant water uses in the Thunder Bay region include those for domestic and industrial water supply, waste disposal, hydro-electric power generation and commercial shipping. The Thunder Bay waterfront is also popular for recreational activities including boating, angling and swimming.

There are two marinas and two yacht clubs in the Thunder Bay inner harbour (formed by a 5 mile breakwall) and a rowing club on the Kaministikwia River. Chippawa Park, located in Mission Bay at the mouth of Whiskey Jack Creek is the primary waterfront recreational area within the city (Figure 2a). The bathing beach there has been closed intermittently over the last several years as a result of high bacterial counts. A considerable number of cottages and several public beaches are located along the north shore outside the city limits. Sibley Provincial Park occupies most of the eastern shore of the bay with other small recreational areas located south of the city. These outlying areas however, have not been impacted by local Thunder Bay inputs.

Commercial fishing had seriously declined at Thunder Bay over several decades beginning with the first fish tainting problem identified in the 1930's. In 1974, the 1971 restriction imposed as a result of high mercury levels in lake trout was lifted. During the following year, whitefish, suckers, lake trout, smelt, menominee, perch, northern pike and burbot were fished extensively. At the same time, sport angling became more important and fishing was better than in the past 20 years.

Water Supply

Municipal water for Thunder Bay is supplied by two water treatment plants. The north plant has a design capacity of 91.0 million litres/day and withdraws water from Thunder Bay through an intake located at Bare Point. The south plant is rated at 77.0 million litres/day and draws water from Loch Lomond located approximately 5.0 km southwest of the mouth of the Mission River. In 1979, the Bare Point pumping station was upgraded to a full filtration plant. The water is chlorinated prior to entering the distribution system. At the Loch Lomond plant, the water is screened, chlorinated and treated with lime before entering the distribution system.

The Ontario Hydro Thermal Generating Station is a 2-unit 300 MW coal-fired operation located on the southeast corner of Mission Island and is the largest individual user of water from Thunder Bay. This station withdraws water from the mouth of the Mission River but only operates intermittently as it is a peak load station.

The second largest user of water in Thunder Bay is the pulp and paper industry which uses lake water for cooling and processing purposes. Abitibi-Price Inc., Fort William Division, Abitibi-Price Inc., Thunder Bay Division, and Provincial Papers Division of Abitibi Price Inc., all withdraw water from Thunder Bay while Great Lakes Forest Products Ltd. withdraws water from the Kaministikwia River. (Figure 2a) The smaller water user industries include Northern Wood Preservers Ltd., Canada Malting Co. Ltd. and Industrial Grain Products which use water from the municipal system.

Waste Disposal

Treated and untreated wastes from industrial and municipal sources are discharged to Thunder Bay both directly and indirectly via the Kaministikwia River (Figure 2a). Thunder Bay is presently serviced by a 109 x $10^3 m^3/d$ (24.0 MGD) primary type wastewater treatment plant which discharges treated effluent to the Kaministikwia River. Phosphorus removal facilities were added to the plant in 1981. The outlying areas rely primarily on septic tank systems.

Specific sources of industrial wastewater loadings to Thunder Bay include the Abitibi-Price Provincial Papers Mill, Abitibi-Price Thunder Bay Division, Abitibi-Price Fort William Division and Great Lakes Forest Products Ltd. Pulp and paper mills are the major industrial dischargers by volume.

Cooling water from the Ontario Hydro thermal generating station is discharged to a relatively shallow area of the Bay through an outfall located at the mouth of the Mission River. When operating at full capacity, the cooling water flow averages 21.6 m^3/s.

Sections of the lower Kaministikwia River, the Mission River and the inner harbour have been dredged each year to maintain navigation depth. Previously, these sediments were disposed offshore near the Welcome Islands (Figure 2). Presently, those dredged sediments which satisfy the open water dredge spoil disposal guidelines (MOE, 1976) are deposited well offshore in Lake Superior, while the contaminated material is disposed of in a confined dredged-spoils disposal facility located in Mission Bay (Figure 2a).

Remedial Measures

In 1983, effluents from the three Abitibi Price mills were meeting existing requirements and new Control Orders were being prepared. Under the Canada-Ontario Pulp and Paper Facility Assistance Program, the company was granted funds to modernize plant production and improve pollution abatement facilities. At the Fort William mill, a primary clarifier was installed in mid-1982 to off-load the lagoon system, and a new pulping facility was installed at the same time, both of which contributed to reducing the overall loading of BOD from the mill. At the Thunder Bay mill, a primary clarifier was installed in late 1981. At the Provincial Papers Division mill, the sulphite pulping process was shut down in mid-1981. These abatement programs reduced the daily combined BOD loading from the three mills to about 35.5 tonnes. All mills were also in compliance with the loading requirements for suspended solids.

The Thunder Bay mill of Great Lakes Forest Products Ltd. was meeting BOD and suspended solids loading requirements as specified in their 1981 Control Order (including the 27 tonnes per day of BOD from the kraft mills). The water pollution abatement programs outlined in the existing Control Order included the following requirements which were completed in 1983: the installation of a cross-recovery system to reduce the loading of BOD discharged from the sulphite mill; an inplant BOD reduction program to further develop closed-cycle processes in both the "A" and "B" kraft mills; and a program to reduce suspended solids loadings from the industrial complex. These programs reduced the total BOD loading by approximately 40 percent (from 1980 to the end of 1983) and ensured compliance with suspended solids requirements.

Phosphorus removal facilities incorporating chemical precipitation became operational at Thunder Bay's Wastewater Treatment Plant early in 1982. In addition to phosphorus removal, improved removal efficiencies for BOD and suspended solids have been achieved. Problems have been encountered in achieving the phosphorus discharge limit; however, remedial work was expected to enable the plant to achieve compliance in 1985.

Bacterial contamination in the inner harbour decreased from earlier investigations as a result of improvements in industrial and municipal sanitary waste discharges and the closing of the North Ward Sewage Treatment Plant in 1978 which previously discharged into the inner harbour via the McIntyre River.

The Provincial Water Quality Objectives with respect to bacteria specific to pulp and paper mill discharges are currently under review. Further remedial actions will depend on the outcome of these reviews.

METHODS

Sample Collection

In the summer of 1983, a water quality study was conducted by the Ministry of the Environment to define the nature and extent of water quality impairment in the Thunder Bay nearshore. Water samples were collected from 60 stations located in the Thunder Bay area (Figure 2). Station locations were fixed with radar and Loran C co-ordinates. Samples were collected over a three day period, July 25 to 27, from the water surface (0.5 m). At several stations, samples were also collected at approximately mid-depth and at 2 m off the bottom.

Physical characteristics (temperature, dissolved oxygen, conductivity and pH) were measured in the field. Depth profiles of water temperature and dissolved oxygen concentrations were also measured and recorded for each sampling location on the first day of sampling to assist in the interpretation of depth effects on water chemistry. Additional data were collected using recording current meters placed at 4 locations (Figure 3) in the nearshore area of Thunder Bay. The meters operated continuously from May 5th to September 17th.

Laboratory Analyses

Water samples were analyzed at the Toronto and Thunder Bay MOE laboratories using standard MOE analytical methods (MOE 1981). Water quality tests included physical characteristics; chemistry; nutrients; microbiology; phenolics; metals; resin, aromatic and fatty acids; and other organic trace contaminants. A complete list of all laboratory analyses performed appears in Table 1.

TABLE 1: LABORATORY ANALYSES PERFORMED ON THUNDER BAY 1983 WATER QUALITY SAMPLES.

Physical Characteristics
turbidity
conductivity (at 25°C)
colour
total suspended solids (S.S.)
total dissolved solids
chemical oxygen demand (COD)
biological oxygen demand (BOD_5)

Nutrients
ammonia
nitrite & nitrate
total phosphorus
total Kjeldahl nitrogen

Chlorophenols
2 - chlorophenol
4 - chlorophenol
2,4 - dichlorophenol
2,3,4 - trichlorophenol
2,4,5 - trichlorophenol
2,4,6 - trichlorophenol
2,3,4,5 - tetrachlorophenol
2,3,5,6 - tetrachlorophenol
2,4,5,6 - tetrachlorophenol
pentachlorophenol

Resin, Aromatic and Fatty Acids
benzoic acid
salicylic acid
phthalic acid
capric acid
lauric acid
myristic acid
palmitic acid
stearic acid
oleic acid
linoleic acid
linolenic acid
arichidic acid
pimaric acid
sandaracopimaric acid
levopimaric acid
palustric acid
isopimaric acid
neoabietic acid
abietic acid
dehydroabietic acid
cinnamic acid
syringic acid
homovanillic acid

Volatile Organohalides
chloroform
carbon tetrachloride
trichloroethylene
bromodichloromethane
tetrachloroethylene
carbonyl sulphide
carbon disulphide
methyl mercaptan
ethyl mercaptan
dimethyl sulphide
dimethyl disulphide
thiophene
hydrogen sulphide
sulphur dioxide

Chemistry
pH
sodium
calcium
chloride
sulphate
dissolved organic carbon
sulphides
reducible sulphur
tannins
cyanide

Microbiology
fecal coliforms
total coliforms
heterotrophic bacteria
pseudomonas aeruginosa
fecal streptococci
escherichia coli
sulphate reducers

Inorganics
iron
silver
aluminium
barium
cadmium
cobalt
chromium
copper
nickel
lead
zinc
arsenic
mercury

PCBs & Organochlorine Pesticides
PCB's
hexachlorobenzene (HCB)
heptachlor
heptachlor epoxide
aldrin
dieldrin
endrin
endosulphan I
endosulphan II
endosulphan sulphate
pp DDE
op DDT
pp DDT
pp DDD
DMDT (methoxychlor)
alpha BHC
beta BHC
gamma BHC (Lindane)
alpha Chlordane
gamma Chlordane
oxychlordane
mirex

Phenolic compounds
guaicol
vanillin
syringaldehyde
acetovanillon
acetosyringone
p-cresol
xylenol
chloro-p cresol
total reactive phenolics

RESULTS AND DISCUSSION

WATER

Physical

Monthly records of current meter data were processed by standard statistical and time series methods (Kohli, 1986). Average monthly current directions and speed for the 4 current meter locations are given in Table 2. Monthly resultant current vectors are presented in Figure 3.

The results indicate that currents are slower and less variable at the northern end of the study area compared to the south. Current directions recorded at location 1409 display the most variation during June and July. Station 1409 was positioned near the mouth of the Mission River and the increased variability recorded there is likely due to the confluence of the river flow and the lake currents.

In general, the results indicate that the bay is flushed from the northeast and that current speeds in July are quite slow when compared to May, June, August and September.

Temperature profiles taken at all stations during the survey indicated stratification on over 80 percent of the sampling occasions. Four inshore stations (139, 680, 663, 799) became unstratified on the third day of sampling (July 27). Wind speed on that day was higher (12.3 km/hr) than on the preceding sampling days (9.9 km/hr and 11.0 km/hr) and daily average current speeds showed an increase as well. Stratification and reduced vertical mixing may account for some surface-subsurface differences in parameter concentrations.

TABLE 2: RESULTANT MONTHLY CURRENT SPEED (cm/sec) AND DIRECTION. (0° as north)

METER LOCATION	MAY	JUNE	JUL 1-28	JUL 28-31	AUG	SEPT
1407 speed	.79	2.01	1.88	4.71	4.69	5.39
direction	200	209	223	223	223	223
1408 speed	17.76	.99	1.63	6.19	4.75	4.14
direction	278	189	185	184	178	181
1409 speed	2.66	1.88	.48	7.66	1.91	2.63
direction	140	95	225	197	198	194
1410 speed	4.10	.37	.05	12.65	2.03	3.65
direction	172	203	201	184	186	179

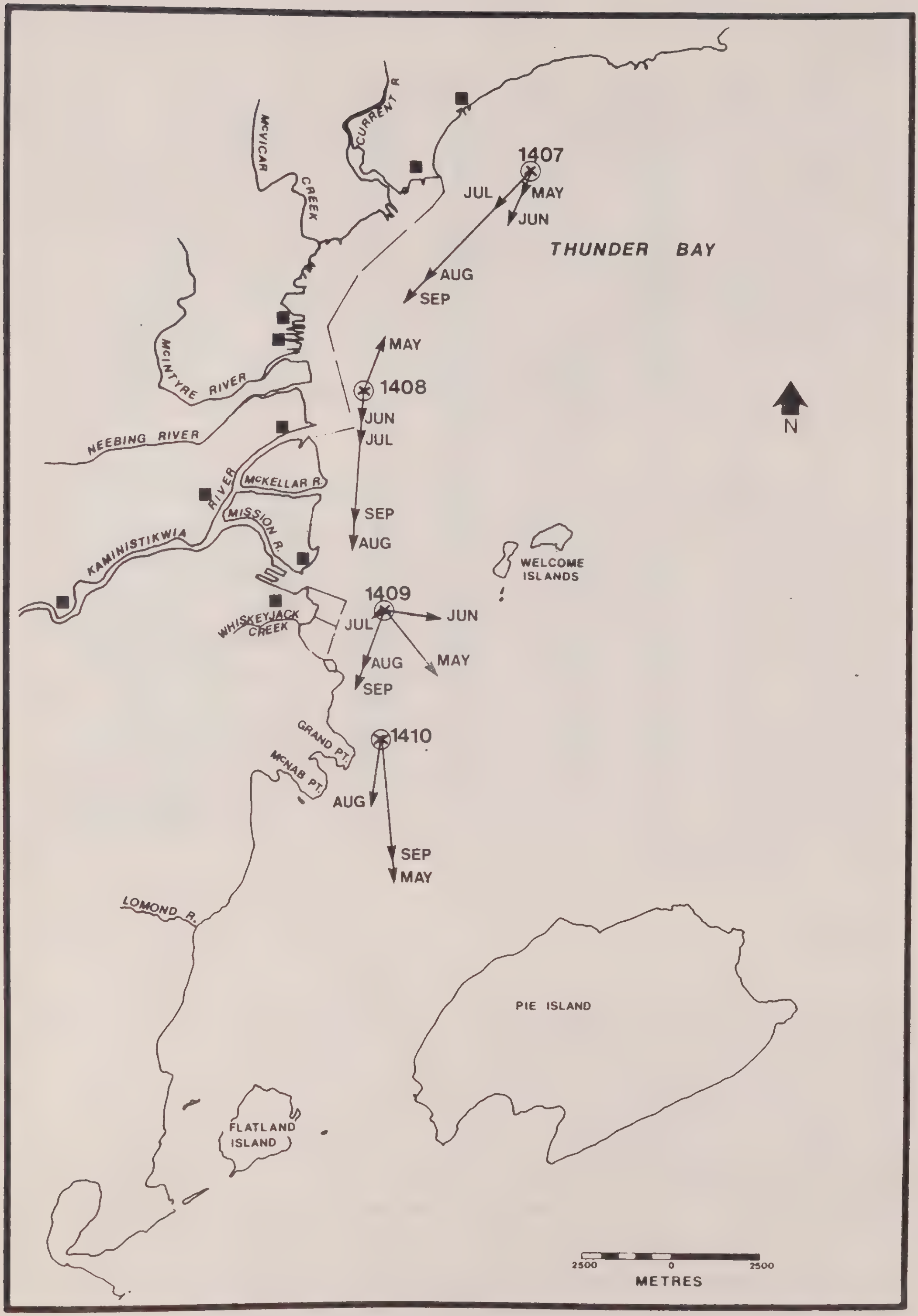


FIGURE 3: RESULTANT CURRENTS, THUNDER BAY, LAKE SUPERIOR, 1983

Chemical

Table 3 gives summary statistics for the routine physical, chemical and microbiological data obtained on July 25 through 27, 1983. Since the arithmetic mean is generally higher than the sample median, the data show a positive skew. This positive skew implies that most of the data are not normally distributed and, hence, does not meet the assumptions of parametric statistics. Therefore, non-parametric statistics or transformed data were used for all analyses presented in this report. Occasional high values and the truncation of the lower end of the distribution for some parameters at the analytical detection limit are likely causes for this positive skew.

Figure 4 depicts the sampling stations found to have elevated concentrations of total phosphorus. Although a firm Provincial Water Quality Objective has not been established, general guidelines of less than 20 ug/L to avoid nuisance concentrations of algae and less than 10 ug/L to protect against aesthetic deterioration have been established (MOE 1984). Twenty-five percent of the sampling stations had average phosphorus concentrations greater than 20 ug/L, primarily in the Kaministikwia River delta and the area near Bare Point. No nuisance algae growths have been identified in Thunder Bay possibly due to limiting factors of the environment (e.g. turbidity, temperature, flow regime, substrate etc.).

Biological

Total and fecal coliform levels were elevated in and around the mouth of the Kaministikwia River at all three outlets and in the harbour area (Figure 5). A potential health hazard may exist for swimming, bathing and other water-contact recreational uses of water if the geometric mean densities for a series (minimum of 10) of water samples exceed 1000 org/100mL total or 100 org/100mL fecal coliforms (PWQO-MOE 1984). Figure 5 shows those stations with individual results in excess of 1000 org/100 mL of total coliforms and 100 org/100 mL of fecal coliforms. These levels were measured at 42 and 56 percent of the sampling stations respectively. Geometric mean densities over the 3-day period, however, were in excess of 1000 org/100mL total and

TABLE 3 THUNDER BAY 1983 DATA SUMMARY

	N	mean	SD[1]	median	UQ[2]	LQ[3]
iron (mg/L)	96	0.126	0.147	0.0565	0.1475	0.027
silver (mg/L)	96	0.0005	0.001	ND	ND	ND
aluminium (mg/L)	96	0.084	0.094	0.0435	0.10725	0.022
barium (mg/L)	96	0.010	0.002	0.009	0.011	0.008
cadmium (mg/L)	96	0.00004	0.00009	ND	ND	ND
cobalt (mg/L)	96	0.0001	0.0003	ND	ND	ND
chromium (mg/L)	96	0.002	0.004	0.001	0.002	ND
copper (mg/L)	96	0.005	0.008	0.004	0.006	0.003
nickel (mg/L)	96	0.0008	0.002	ND	0.001	ND
lead (mg/L)	96	0.009	0.028	0.003	0.00775	ND
selenium (mg/L)	83	0.001	0.001	ND	ND	ND
zinc (mg/L)	96	0.002	0.002	0.001	0.003	ND
chemical oxygen demand (mg/L)	172	16.52	13.02	13	22	8
ammonia (mg/L)	172	0.018	0.030	0.01	0.01	0.01
nitrite + nitrate (mg/L)	172	0.232	0.055	0.25	0.26	0.23
sulphate (mg/L)	95	5.92	3.19	4.5	6.17	4.14
sulphate reducers (org/100 mL)	95	100*		75	460	23
arsenic (mg/L)	45	0.001	0	0.001	0.001	0.001
cyanide (mg/L)	43	0.001	0	0.001	0.001	0.001
total suspended solids (mg/L)	168	2.45	1.91	2	3	1
sodium (mg/L)	172	4.15	4.40	2.5	3.9	2.125
chloride (mg/L)	171	3.27	2.02	2.4	3.6	2.1
temperature (°C)	164	16.99	2.93	17.5	18.5	15.9
dissolved oxygen (mg/L)	159	9.20	1.61	9.6	10	8.8
conductivity (umo/cm)	168	107	11.2	102	110	100
pH	169	7.50	0.26	7.6	7.7	7.4
BOD_5 (mg/L)	169	1.35	0.92	1	1.45	0.85
turbidity (FTU)	173	1.17	1.00	0.7	1.65	0.45
total phosphorus (mg/L)	172	0.015	0.018	0.008	0.018	0.0043
Kjeldahl nitrogen (mg/L)	171	0.26	0.12	0.22	0.29	0.19
mercury (ug/L)	98	0.09	0.05	0.05	0.11	ND
phenols (ug/L)	174	1.53	4.01	0.2	0.8	0.2
dissolved organic carbon (mg/L)	93	4.10	3.32	2.8	3.9	2.3

[1] SD - Standard deviation
[2] UQ - Upper (75%) quantile
[3] LQ - Lower (25%) quantile
* Geometric mean

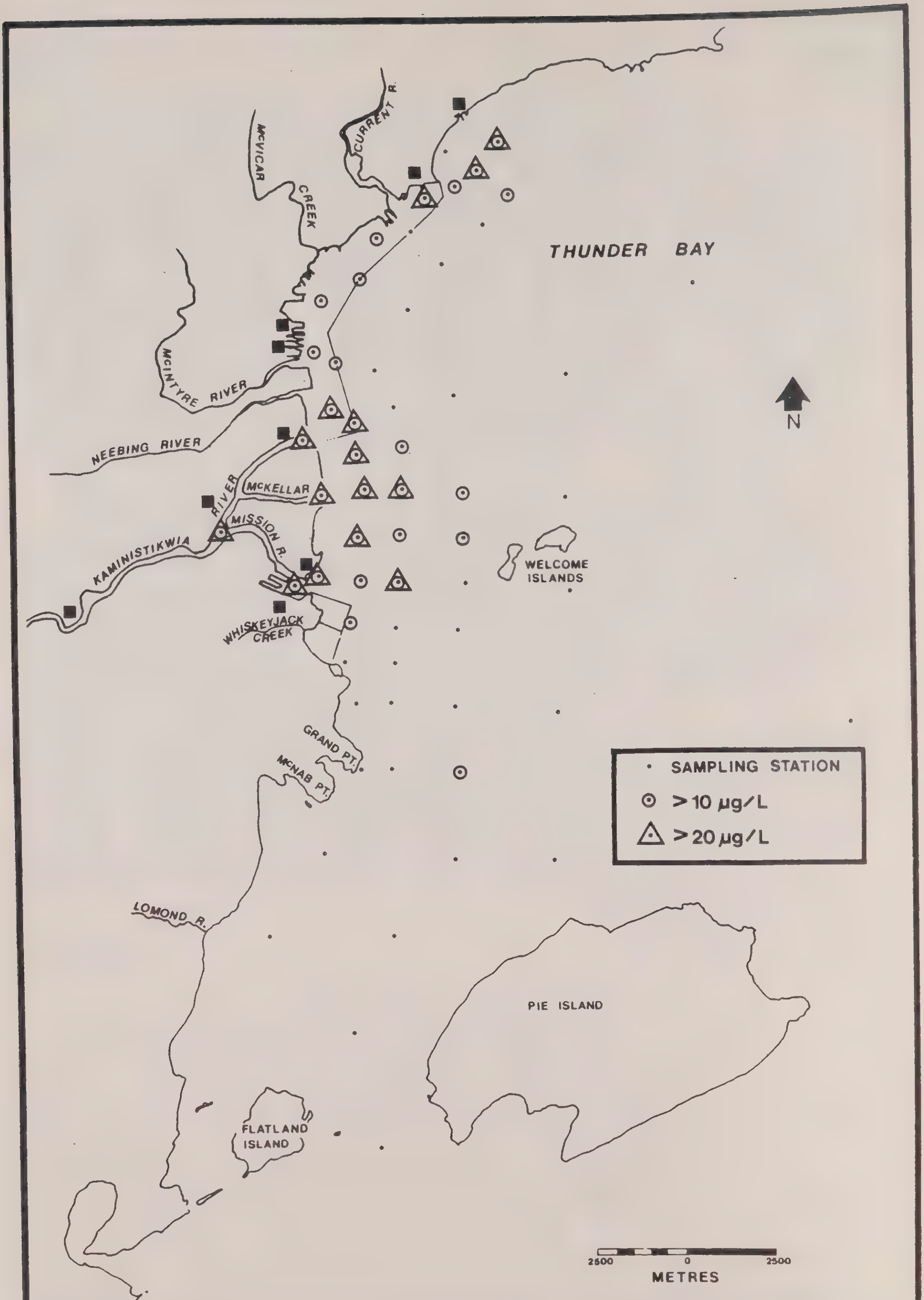


FIGURE 4 : SAMPLING STATIONS WITH ELEVATED LEVELS OF TOTAL PHOSPHORUS

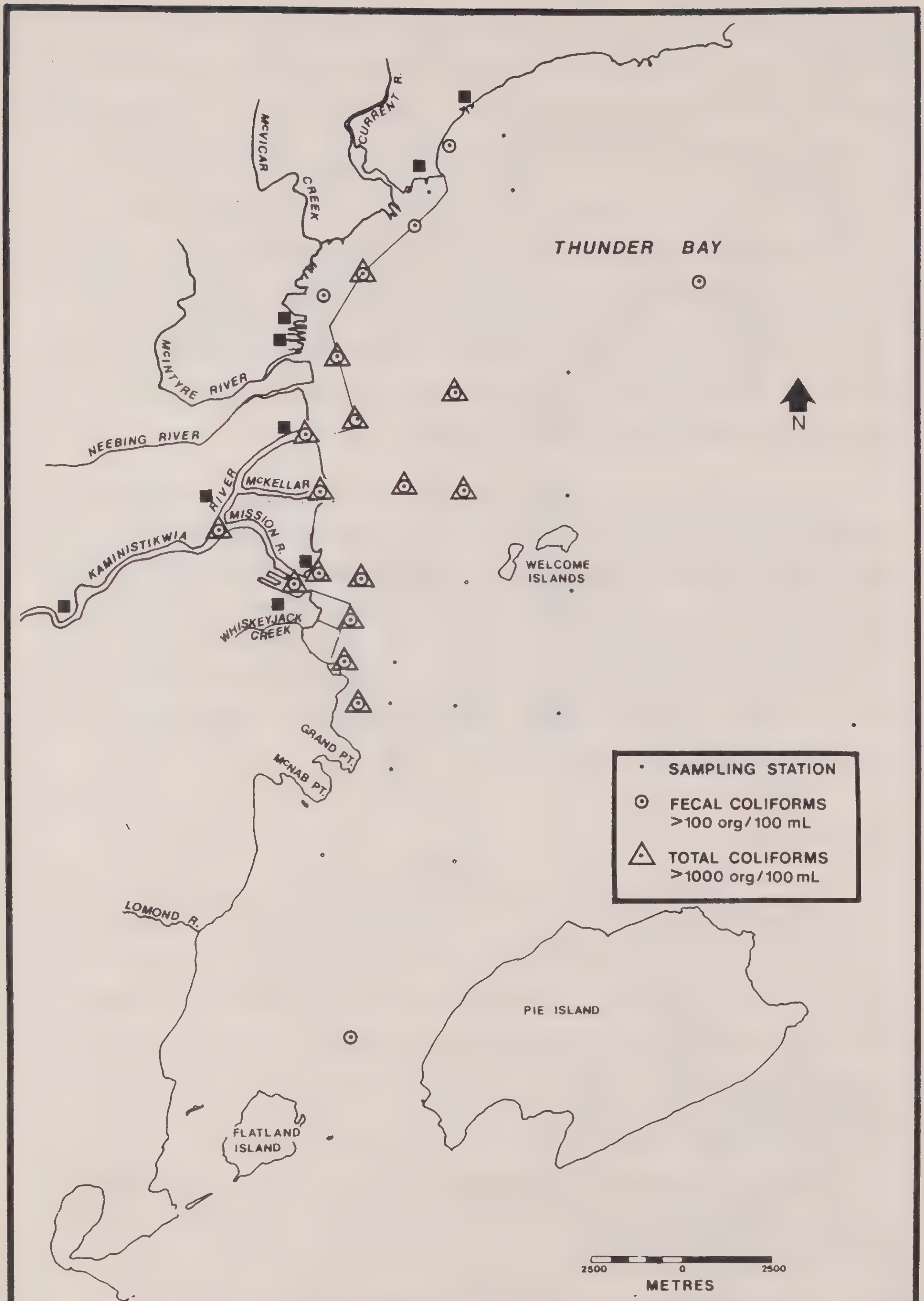


FIGURE 5: SAMPLING STATIONS WITH ELEVATED LEVELS OF FECAL AND TOTAL COLIFORMS

100 org/100mL fecal coliforms at only 10 and 18 percent of the stations, respectively, in an area near the Kaministikwia River mouth and along the shoreline. Speciation of fecal coliforms for Klebsiella, a bacterium associated with pulp and paper mill effluent, was not part of the laboratory analysis for this study. However, given the analytical techniques employed it is possible for reported fecal coliform counts to contain some (or all) Klebsiella bacteria. There are no Provincial Water Quality Objectives for Klebsiella at present and no agreement on the human health implications of Klebsiella in water. Future studies should determine whether fecal (animal or human) (municipal sources) or Klebsiella bacteria (industrial sources) are cause for concern in the Thunder Bay area.

Water contact sports and activities in Thunder Bay are limited because of waterfront inaccessibility and cold water temperatures. In Mission Bay however, Chippawa Park, the primary waterfront recreational area within the city, has been affected by high bacteria levels and has been subject to beach closings on occasion. The north shore and some areas south of the city are more likely to be used for swimming or water contact recreation however these areas did not appear to be affected by bacterial contamination.

Trace Organics

PCBs and most organochlorine pesticides (with the exception of alpha BHC (hexachlorocyclohexane)) were detected only occasionally and in trace amounts at a limited number of stations (Figure 6). Most of these stations extend in a band north-east from Grand Point. However, alpha BHC was detected throughout the study area in 71% of the samples taken (Table 4) with reported levels ranging from less than 1 ng/L to 7 ng/L. Lindane (gamma BHC), a pesticide not actively used in Ontario, isomerizes to alpha BHC by biological processes (EPA, 1979). There are no criteria established for alpha BHC in water at present and little information is available on what levels are cause for concern in the aquatic environment.

No PCB's, organochlorine pesticides or chlorophenols were found in the inner harbour with the exception of alpha BHC. Only two stations

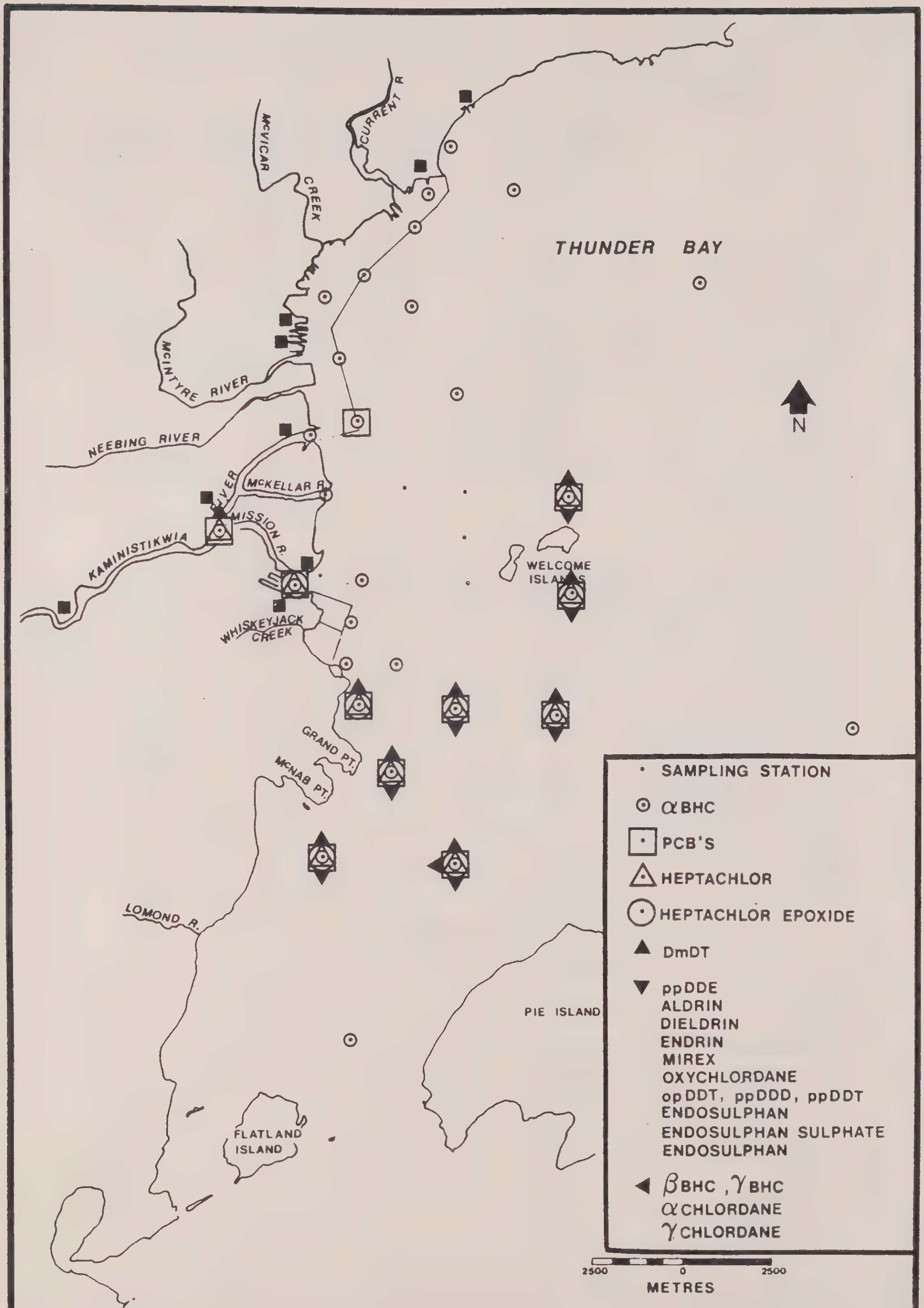


FIGURE 6: SAMPLING STATIONS WITH DETECTABLE LEVELS OF PCB'S/ORGANOCHLORINES

TABLE 4: PCB's/organic compounds, resin, aromatic and fatty acids detected in Thunder Bay, 1983

COMPOUNDS DETECTED	NO. OF SAMPLES	No. DETECTED	% DETECTED	DET. LIMIT
PCB	41	10	24	20 ng/L
heptachlor	41	10	24	1
aldrin	41	8	20	1
pp DDE	41	9	22	1
mirex	41	8	20	5
alpha BHC	41	29	71	4
oxychlordane	41	8	20	2
op-DDT	41	8	20	5
pp-DDD	41	8	20	5
pp-DDT	41	8	20	5
DMDT-methoxychlor	41	9	22	5
heptachlor epoxide	41	9	22	1
endosulphan I	41	8	20	2
dieldrin	41	8	20	2
endrin	41	8	20	4
endosulphan II	41	9	22	4
endosulphan sulphate	41	8	20	4
beta BHC	41	1	2	1
gamma BHC	41	1	2	1
Chlordane alpha	41	1	2	2
Chlordane gamma	41	1	2	2
2,4,6-trichlorophenol	41	14	34	50
2,4,5-trichlorophenol	41	8	20	50
2,3,4-trichlorophenol	41	9	22	100
2,3,5,6-tetrachlorophenol	41	8	20	50
2,3,4,5-tetrachlorophenol	41	8	20	50
pentachlorophenol	41	9	22	50
chloroform	15	13	87	0
Aromatic acids				
benzoic acid	15	1	7	2 ug/L
Fatty acids				
myristic acid	15	9	60	1
palmitic acid	15	13	87	1
oleic acid	15	5	33	2
stearic acid	15	3	20	2
linoleic acid	15	2	13	4
Resin acids				
pimaric acid	15	13	87	1
sandaracopimaric acid	15	3	20	1
levopimaric acid	15	1	7	1
palustric acid	15	3	20	1
isopimaric acid	15	4	31	1
neoabietic acid	15	2	13	1
abietic acid	15	4	31	1
dehydroabietic acid	15	10	67	1

in the Mission and lower Kaministikwia Rivers had measurable amounts of PCB's or organochlorine pesticides (alpha BHC, heptachlor, heptachlor epoxide, Methoxychlor (DMDT). Table 5 lists organic compounds found to be in excess of Provincial Water Quality Objectives.

Levels of chlorophenols in the Thunder Bay area were all found to be less than Provincial Water Quality Objectives (MOE, 1985). Some chlorophenols in trace amounts (up to 230 ng/l-2,4,6-trichlorophenol) were detected at the same stations extending in a band northeast from Grand Point (Figure 7). The four pulp and paper mills in Thunder Bay are the most likely contributors. Results of a 1983 Inventory of Pulp and Paper Effluent constituents in Lake Superior observed tri, tetra and pentachlorophenols in effluents from the Thunder Bay mills (Cherwinsky & Murray, 1986).

Current meter results for the three-day water quality survey period indicated a northward current at location 1410 near Grand Point (Figure 3). No current direction is available for location 1409 on these dates. The uncharacteristic pattern at location 1410 may possibly suggest a source of chlorophenols and trace organics other than the industrial discharges to the water body. The area near the Welcome Islands has historically (pre-1965) been used for open water disposal of dredged material, constituting a potential source of contaminants in these locations (Figure 2a). The 1974 Canada-USA Great Lakes Water Quality Agreement and the establishment of open water disposal guidelines for dredged material (Persaud & Wilkins, 1976) ended any previous indiscriminate dumping of sediments in open waters. Dredging operations now include sampling for contaminants and confined or semi-confined disposal of contaminated sediments. Atmospheric contributions of PCB's and trace organics to Thunder Bay have also been documented and may be responsible for low levels of these compounds observed in surface waters remote from any known source (Eisenreich et al, 1979).

All three outlets of the Kaministikwia River had measureable levels of phenolic compounds; 2,4,6-trichlorophenol was the most commonly occurring form (Table 4) and levels up to 560 ng/L were observed in the lower Kaministikwia River at station 802. Total phenol

TABLE 5: ORGANIC AND INORGANIC CONCENTRATIONS (ug/L) IN EXCESS OF PROVINCIAL WATER QUALITY OBJECTIVES (PWQO)

Parameter	PWQO	% >PWQO	Maximum	Station
iron (ug/L)	300	14	600	802
aluminum (Guideline) (ug/L)	100	24	520	680
cadmium (ug/L)	0.2	4	5	682
copper (ug/L)	5	30	84	677
PCB's (ng/L)	1	24	145	176
mirex (ng/L)	1	20	5	*
endrin (ng/L)	2	20	4	*
heptachlor + heptachlor epoxide (ng/L)	1	22	9	176
total DDT (ng/L)	3	20	16	*
DMDT-methoxychlor (ng/L)	40	2	60	802
endosulphan (ng/L)	3	22	10	*
aldrin + dieldrin	1	20	3	*

* Maximum values observed at detection limit at several stations.

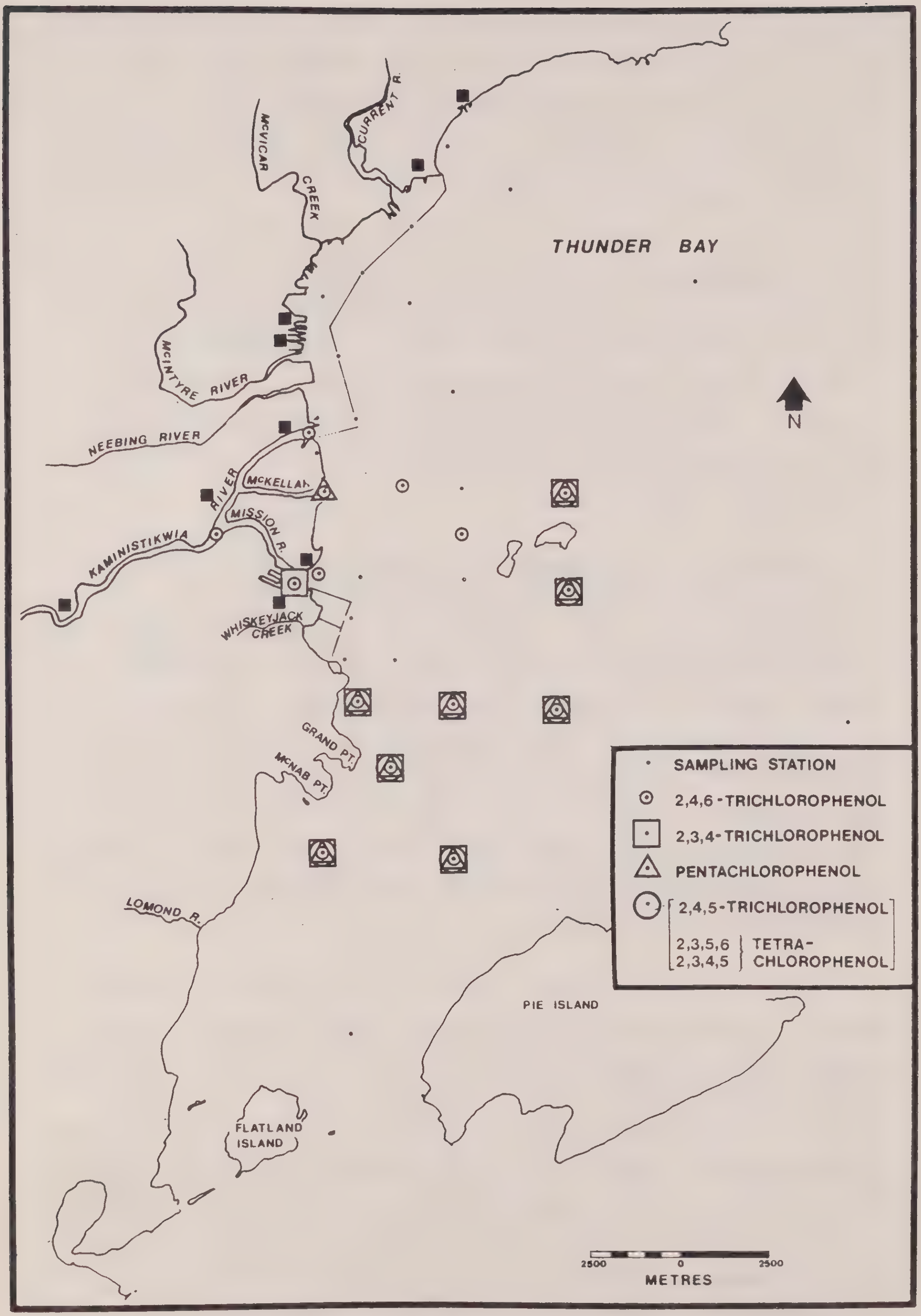


FIGURE 7: SAMPLING STATIONS WITH DETECTABLE LEVELS OF CHLOROPHENOLS

concentrations were also highest at this location at a maximum of 28.8 ug/L. 2,4,6-Trichlorophenol is used in the manufacturing of wood preservatives as well as fungicides, bacteriacides, and as an anti-mildew agent for textiles. A Water Quality Objective based on toxicity to aquatic organims has been established for trichlorophenols at 18 ug/L (18000 ng/L) (MOE, 1985).

Chlorophenols may enter the environment in industrial and municipal effluents, through agricultural application and from the disposal of wastes containing chlorophenols. Chlorophenols or chlorinated phenols may also be produced in situ. Chlorine used in wastewater treatment will react with phenols producing chlorinated phenols by replacing hydrogen atoms with chlorine atoms on the phenol molecule (MOE, 1985).

The toxicity of chlorophenols in general, increases with increasing chlorine substitutes, pentachlorophenol with five chlorines being the most toxic isomer. Measured and calculated bioconcentration factors for the higher chlorinated phenols have also indicated a greater tendency to bioaccumulate in aquatic biota. The higher chlorinated phenols will adsorb onto sediments and particulate matter more readily and biodegrade at a slower rate than the lower chlorinated phenols as well. Possible dioxin contamination of pentachlorophenol and trichlorophenol also poses an environmental threat, even at low levels due to persistence, toxicity and the potential for bioaccumulation (MOE, 1984).

Resin, aromatic and fatty acids were found primarily around the mouth of the Kaministikwia River and also in the inner harbour and extending to just south of Whiskey Jack Creek. (Figure 8). Detectable levels of dehydroabietic acid and palustric acid at station 791 offshore and palmitic, pimaric and abietic acids at station 798 between Flatland and Pie Islands, as well do not appear to originate from an obvious source. All of the above acids have no guidelines established as yet for levels in the aquatic environment. Resin acid soaps from pulp and paper mill discharges present a serious problem, however, from both a toxic and quantitative standpoint. Softwoods (particularly pine) contain substantial amounts of resin and some studies have

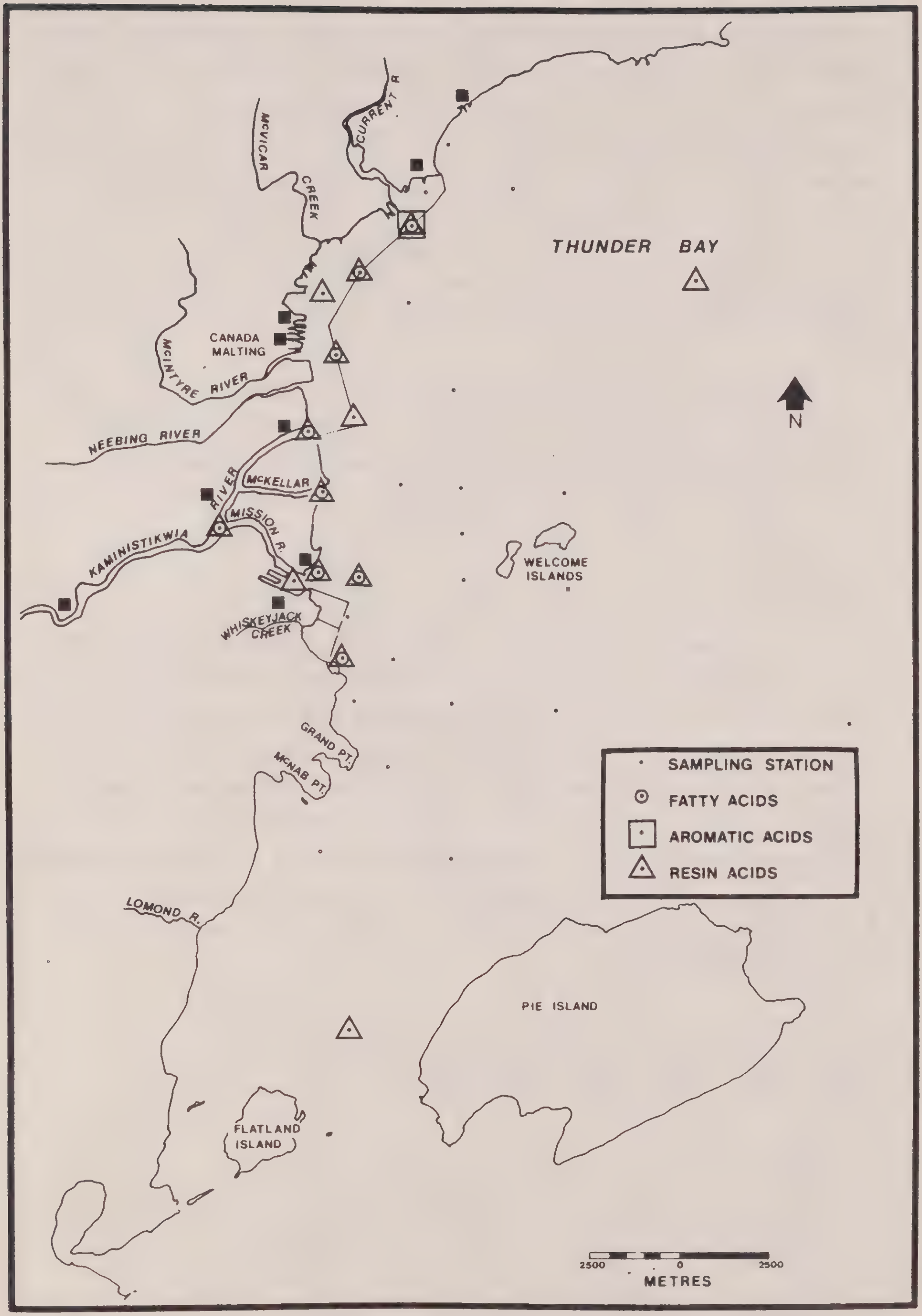


FIGURE 8: SAMPLING STATIONS WITH DETECTABLE LEVELS OF FATTY, AROMATIC AND RESIN ACIDS

indicated that resin acid soaps are the most likely candidates of known composition to be present in the final effluent in concentrations high enough to affect the LC50 values. LC50 values range from 0.7 to 1.6 mg/L depending upon the specific resin soaps involved (IJC, 1981) maximum levels in ambient water during this study were 29 ug/L in the Kaministikwia River (Stn 802) for abietic and dehydrobietic acid. Their toxic effect is limited to gilled organisms as opposed to poisons that are ingested and build up in the food chain. The half-life of dehydroabietic acid in the water column is about 6 weeks (IJC, 1981).

Our present knowledge of the significance and fate of resin acids in the aquatic environment is inadequate. Studies are underway to establish Water Quality Objectives and effluent limits based on the most sensitive of water uses, the protection of aquatic life.

Inorganics

Observations of total metal concentration throughout the western nearshore portion of the bay, based on percentage of occurrence, are given in Table 6. Several station locations exceeded the 1978 Water Quality Objectives for iron, cadmium, aluminium (Guideline) and copper (Figure 9) (Table 5). Over 30% of the stations sampled had copper levels in excess of the Provincial Water Quality Objective (5 ug/L) and these were found scattered throughout the nearshore. Background copper levels, however, have been observed in the Kaministikwia River consistently higher than the PWQO (J. Vander Wal, Northwestern Region, personal communication).

TABLE 6: Metals detected in Thunder Bay water quality samples, 1983

METALS DETECTED	NO. OF SAMPLES	NO. DETECTED	% DETECTED
iron	96	96	100
silver	96	9	9
aluminium	96	95	99
barium	96	96	100
cadmium	96	14	15
cobalt	96	10	10
chromium	96	52	54
copper	96	96	100
nickel	96	39	41
lead	96	50	52
selenium	83	9	11
zinc	96	59	61
mercury	98	52	53

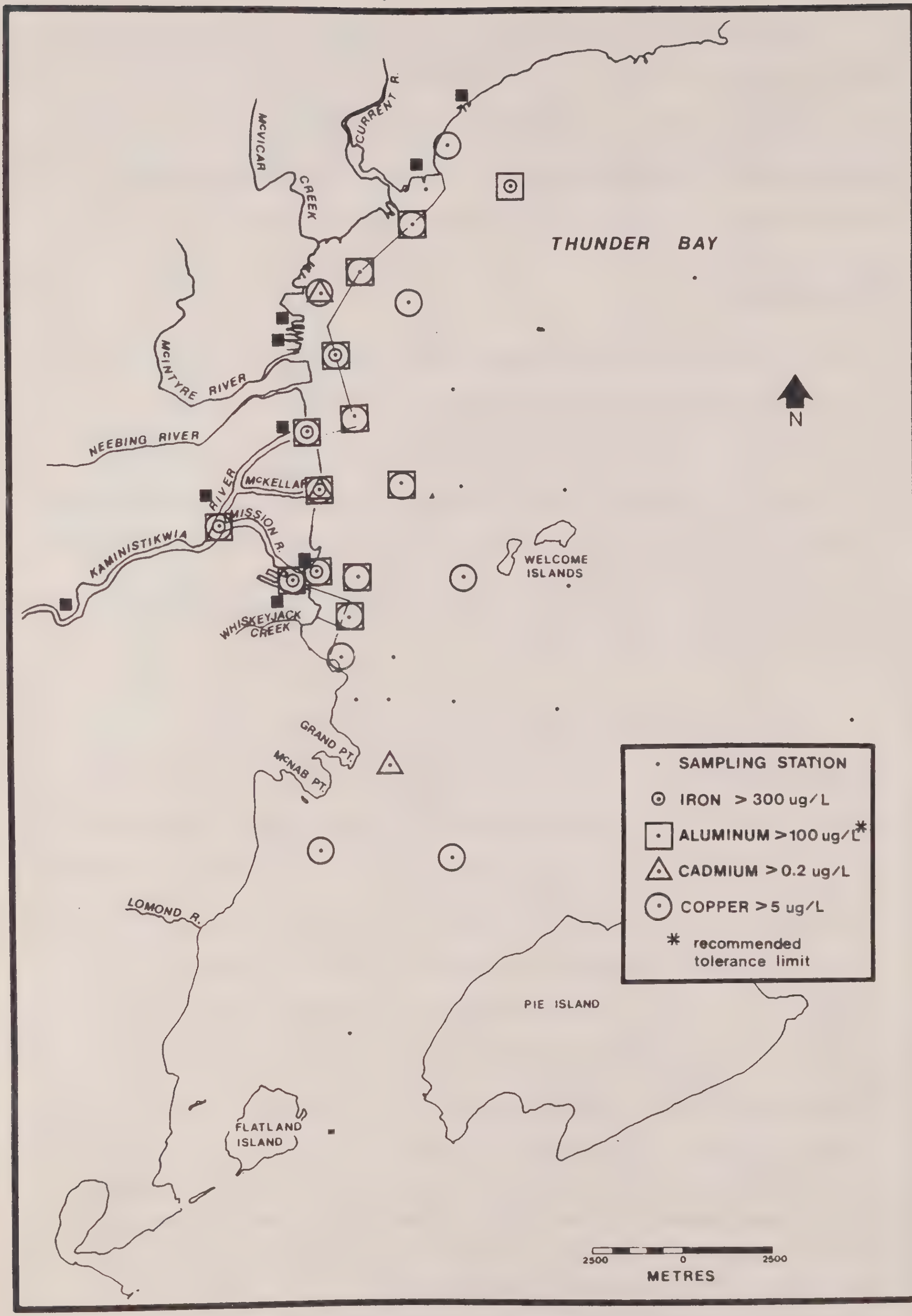


FIGURE 9: SAMPLING STATIONS WITH OBSERVED LEVELS OF METALS EXCEEDING PROVINCIAL WATER QUALITY OBJECTIVES

Concentrations of these metals were highest in the Kaministikwia River outlets. Possible sources include industrial and municipal effluents entering the river and storm sewer inputs as well as the natural background inputs. Barium and the above four metals were detected with the most consistency. The other heavy metals, when detected, were at concentrations below Objective levels.

Depth Variation

The water quality data were analyzed to assess the spatial and temporal variation in the water chemistry on several scales. Differences between surface and subsurface values for three parameters (temperature, conductivity, and turbidity) were examined using data from stations sampled at several depths. These parameters are expected to reveal the vertical variability to be found in the nearshore since they closely reflect physical conditions in the water column. Data from ten stations with depths varying from 3m to 10m were used for visual comparisons (Table 7).

Limited data were available at varied depths. However, temperature, conductivity and turbidity levels were generally higher in surface samples than in subsurface samples. All of the ten inshore stations were found to be stratified upon examination of temperature profiles recorded during the survey. As well, a phenomenon of layering of water at the Kaministikwia River mouth has been documented and is described in terms of warm river water flowing out over the colder lake water, resulting in reduced vertical mixing and an increased probability of significant differences in parameter concentrations (MOE, 1972). Although surface waters inshore at Thunder Bay likely contain the highest contaminant levels, it would be worthwhile in future surveys to gain more information on the mixing of river and lake waters and the vertical gradation further from shore. This will assist in determining the fate of the contaminants entering open water and provide some measure of the impact of the Kaministikwia River on the water quality in Thunder Bay. Results of a 1985 survey by MOE, when available, will provide this information.

TABLE 7: DIFFERENCES BETWEEN DEPTHS OF SAMPLING, SURFACE AND SUBSURFACE

Temperature (C)		Conductivity (umos/cm)		D.O. (mg/L)		Turbidity (FTU)	
Surface	Subsurface	Surface	Subsurface	Surface	Subsurface	Surface	Subsurface
21.7	12.8	108	100	4.7	9.2	1.6	0.6
21.2	11.6	104	102	6.6	8.2	1.8	1.4
20.9	16.5	112	102	4.8	4.2	0.95	1.7
17.1	14.1	104	102	12	12	1.8	0.8
20.1	21.0	162	102	4.3	6.7	1.2	0.8
17.2	12.7	146	102			4.0	1.7
16.2	12.1	138	101			2.7	2.6
21.9	14.2	123	114			3.8	2.6
21.8	11.2	102	104			2.2	0.85
		103	102			0.65	0.65
		147	115			1.2	0.6
		142	114			3.1	1.9
		122	103			2.6	1.7
		123	128			3.2	0.85
		119	119			6.2	3.1
		119	108			1.8	2.7
		104	108			2.8	2.6
		139	102			1.4	1.4
		101	101			3.7	2.4
		110	103			0.6	0.64
		107	102			1.6	0.75
		110	104			1.7	1.5
		109	103			1.6	1.8
		104	104			2.0	1.9
		109	108			0.7	0.7
		101	102			1.3	1.3
		155	110			0.85	0.7
		140	110			4.1	3.3
						3.3	3.5
						4.4	4.1

Covariation

Spearman rank correlation coefficients for specific parameters from each station were computed to illustrate the interrelationships among the variables. The relationship between the paired variables may be assessed using the Spearman coefficients and the variables need not show a bivariate normal distribution as is required for significance tests using Pearson's product-moment correlation coefficient (r)(Conover, 1971). The coefficients and significance levels appear in Table 8. Many parameters were significantly correlated implying that they have similar spatial-temperal patterns. Mercury was a noticeable exception. Generally, the highest degree of correlation between parameters was with the non-metals. Because of the smaller sample size, metals were omitted from a further analysis of correlation using principal components.

The spatial/temporal patterns of the parameters were examined using principal components analysis (PCA). PCA is a multivariate technique which identifies patterns of shared variation among parameters while retaining as much of the information as possible from the original data set. Using this technique, it is possible to identify those parameters with similar spatial/temporal patterns and to represent those patterns by new variables or components. Each component represents one spatial/temporal pattern and consists of a linear combination of the original variables. Input to the analysis consisted of measurements of 15 conventional parameters at 60 sampling locations. The analysis was based on a correlation coefficient.

The first principal component accounted for 60.7% of the total variance in the original data set. The efficiency of the summarization is illustrated by the fact that each original parameter represented on average only 6.7% (i.e. 1/15) of the total variance in the original data set. The results indicated that 9 of the 15 parameters used in the analysis (turbidity, pH, BOD, conductivity, dissolved oxygen, total Kjeldahl nitrogen, nitrite + nitrate, phenols and chloride) were highly correlated over time and space. The first component accounted for more than 50% of the variance of each of these parameters. The remaining components are not shown since they did not identify interpretable

TABLE 8: SPEARMAN RANK CORRELATION COEFFICIENTS, THUNDER BAY WATER QUALITY, 1983

	Fe	Al	Ba	Cu	COD	NO2+NO3	S.red.	SSO4	S.S.	Na	Cl	temp	DO	cond	BOD_5	turb	phos	Kjeld	Hg	FC	TC
iron	1	.96**	.84**	.53**	-.14	.21*	-.24	-.11	-.22*	-.31**	-.31**	.06	.42**	-.33**	-.24*	-.27*	-.22*	-.26*	-.09	-.18	-.33
alum		1	.84**	.44*	-.13	.17	-.23	-.08	-.16	-.26*	-.27	-.05	.40**	-.29**	-.20	-.24*	-.22*	-.22*	-.09	-.19	-.34*
barium			1	.47*	-.15	.21*	-.22	-.05	-.10	-.27**	-.24*	-.09	.37**	-.27**	-.21*	-.20	-.11	-.20	.03	-.22	-.30*
copper				1	.01	.16	-.23	-.26	-.09	-.21*	-.24*	-.06	.31**	-.22*	-.15	-.11	-.13	-.20	-.07	-.26	-.23
COD					1	-.51*	.63*	.62**	.27**	.53**	.46**	.30**	-.41**	-.52**	.49**	.51**	.45**	.46**	.13	.62**	.59**
NO2+NO3						1	-.87*	-.63**	-.53**	-.78**	-.84**	-.55**	.67**	-.82**	-.61**	-.74**	-.45**	-.75**	-.14	-.72**	-.70**
sulphate reducers							1	.73**	.55**	.93**	.92**	.65**	-.81**	.96**	.78**	.89**	.77**	.88**	.17	.82**	.83**
sulphate								1	.43**	.73**	.57**	.28**	-.47**	.74**	.69**	.80**	.77**	.61**	.21*	.74**	.78**
S.S.									1	.52**	.53**	.12**	-.35**	.59**	.37**	.58**	.44**	.56**	-.04	.53**	.51**
sodium										1	.86**	.40**	-.66**	.89**	.72**	.84**	.60**	.78**	.15	.80**	.83**
chloride											1	.54**	-.76**	.92**	.60**	.82**	.53**	.79**	.10	.76**	.74**
temp												1	-.64**	.42**	.40**	.27**	.09**	.41**	.09	.35**	.27*
DO													1	-.69**	-.57**	-.57**	-.25**	-.64**	-.16	-.54**	-.53**
cond														1	.72**	.93**	.66**	.85**	.17	.84**	.84**
BOD_5															1	.70**	.53**	.66**	.13	.61**	.66**
turb																1	.73**	.79**	.20	.80**	.85**
phosphorus																	1	.68**	.22*	.73**	.78**
Kjeldahl																		1	.18	.72**	.70**
mercury																			1	.20	.27*
fecal coliforms																				1	.82**
total coliforms																					1
phenols																					
DOC																					

patterns. The scores for the sampling locations on the first component reflect the spatial patterns in the conventional parameters as described above. Figures 10, 11 and 12 illustrate the spatial pattern of the principal component scores for each day of sampling. The patterns in the scores were used as a guide in the construction of zones of water quality impairment which are described later in the report.

Spatial Variation

Describing water quality in nearshore areas poses a difficult question and approaches range from station by station descriptions to combining all results to provide overall "average" conditions. Treating the entire area as a homogeneous unit is an inadequate approach. Shoreline currents, wind and wave effects, river and stream inflow, industrial and municipal outfalls, are all factors affecting the distribution of chemicals and nutrients in the water column. Individual station results for a large survey, unless grouped in some way, reduce the researcher's ability to draw comparisons and make conclusions and recommendations for large areas. In order to determine the best approach for characterizing the 1983 Thunder Bay nearshore water quality, a series of tests were performed on physical data, nutrients and metals using different groupings of stations. These groups or zones were created either arbitrarily or based on previously used zonation patterns in the Thunder Bay waterfront.

Differences among zones were examined using a Kruskal Wallis test. This test uses ranks of observations rather than raw data and is a non-parametric analogue of the ANOVA (Sokal & Rohlf, 1969). Using this method, it is possible to determine whether individual stations in the group tend to have a disproportionate number of high or low observations. All of the data for a parameter are ranked from low to high, then a t-statistic is calculated. If group sample sizes are greater than 5, then t is approximately distributed as a Chi-square statistic with k-1 degrees of freedom. If t is large, (i.e. exceeds the 0.95 quantile of a Chi-square distribution with k-1 degrees of freedom) then the null hypothesis of equal station means (no difference between stations) can be rejected.

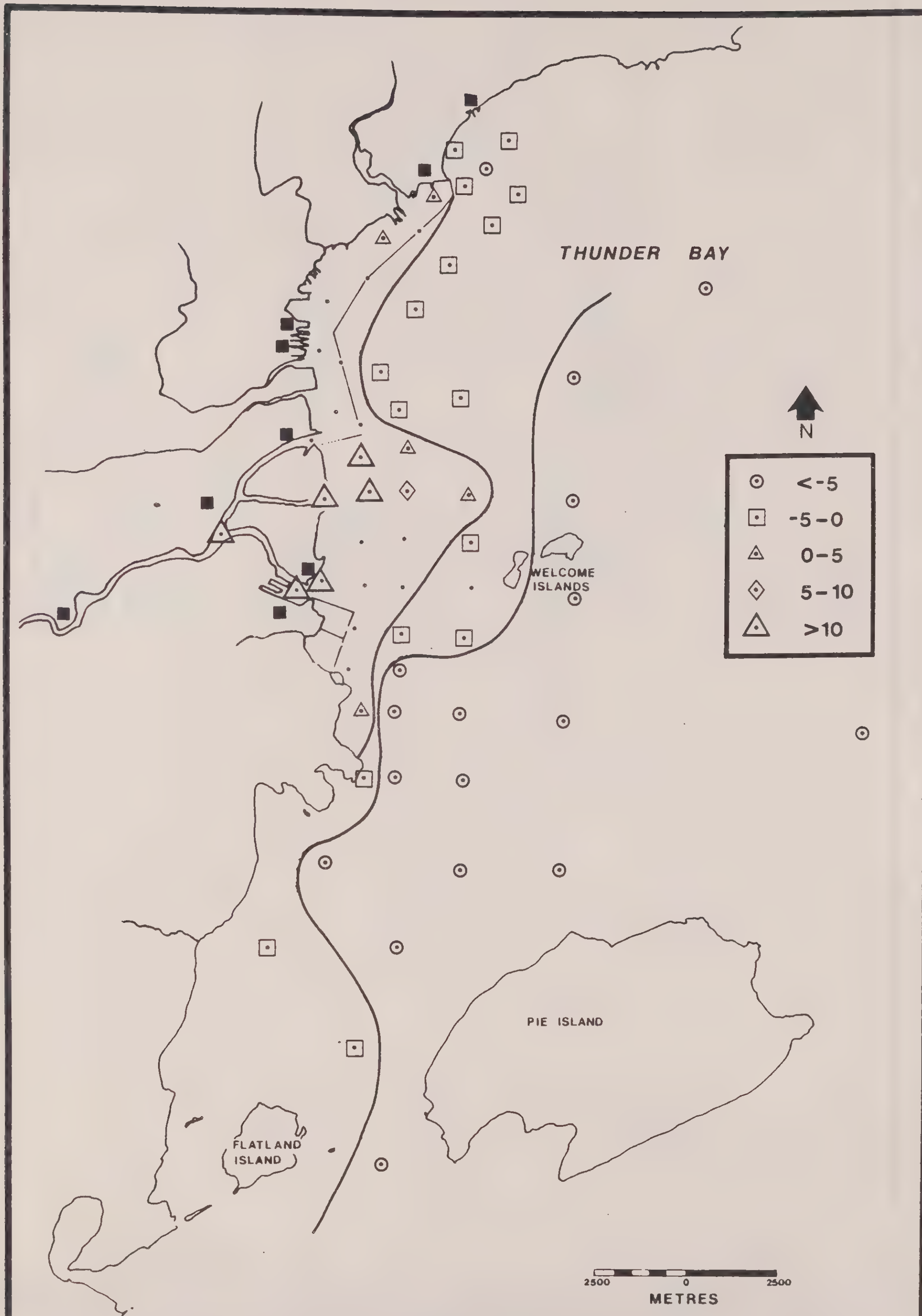


FIGURE 10: PRINCIPAL COMPONENT SCORES, JULY 25, 1983

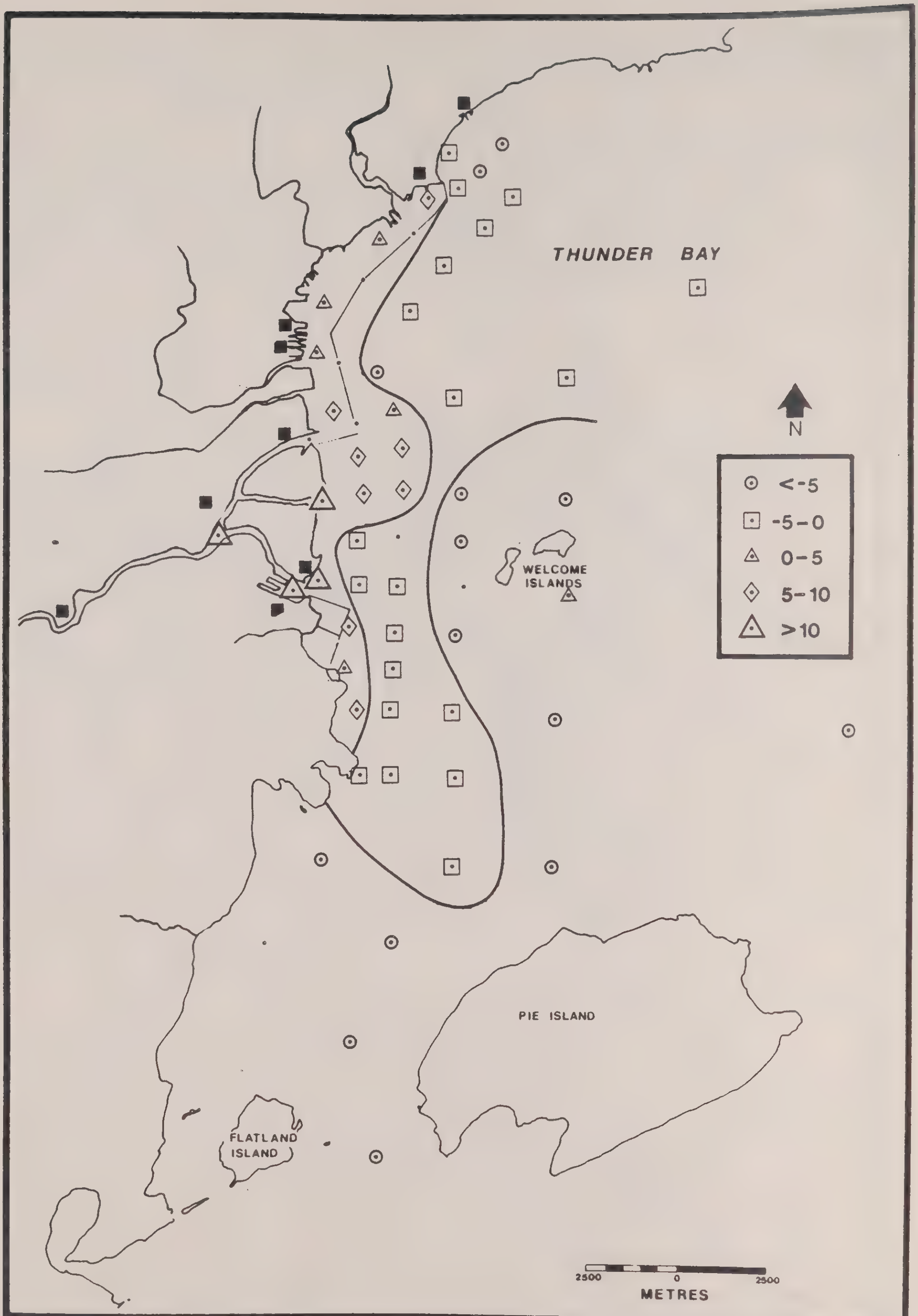


FIGURE 11: PRINCIPAL COMPONENT SCORES, JULY 26, 1983

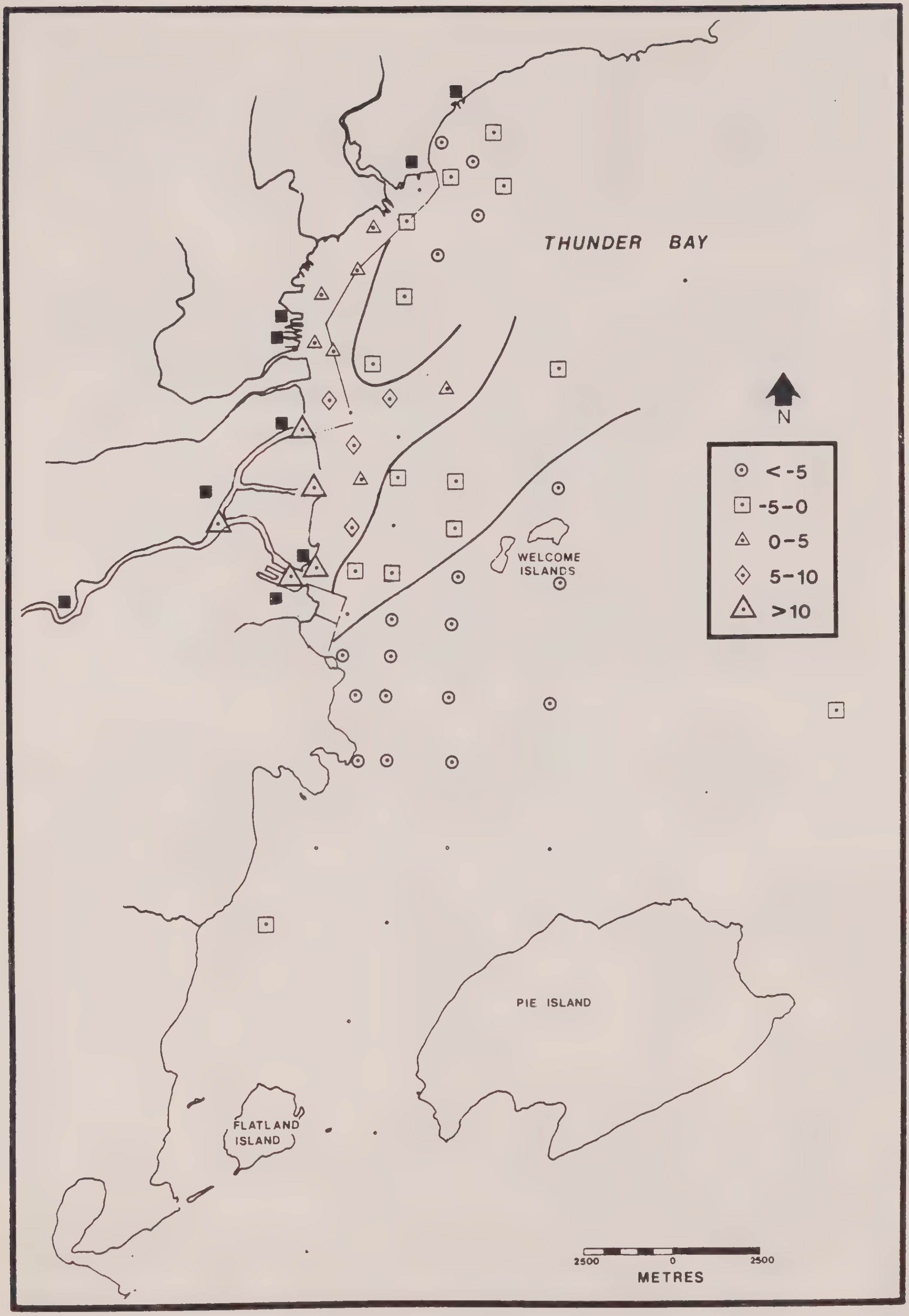


FIGURE 12: PRINCIPAL COMPONENT SCORES, JULY 27, 1983

In the Thunder Bay Regional water quality survey of 1970 (MOE, 1972), 3 zones were used for comparative purposes; 1) river stations, 2) inner harbour stations, and 3) outer harbour stations. In 1974, the area was divided up into zones A, B, C, D which ran outward from the shore in parallel rows.

A Mann Whitney U test (a non-parametric test used when comparing only 2 groups of data) was used to compare 1983 data grouped according to the 1970 zonation. The 'river' zone 1 was omitted due to lack of comparable 1983 data. Significant differences were evident between the inner and outer harbour stations for iron, aluminium, barium, copper, suspended solids, conductivity, turbidity, phosphorus and total Kjeldahl nitrogen. Of all the parameters tested, temperature was the exception, in that no significant differences were evident (Table 9). When the zonation pattern used in 1974 (A, B, C, D) was applied to the 1983 data using a Kruskal Wallis test, all parameters tested (as above), except copper, differed significantly among the zones.

TABLE 9: AMONG-ZONE TEST SCORES FOR SPATIAL COMPARISONS OF THUNDER BAY 1983 DATA

	1970 ZONES MANN WHITNEY U SCORES	1974 ZONES KRUSKAL WALLIS SCORES (DF=3)	NORTH/SOUTH/ OFFSHORE ZONES KRUSKAL WALLIS SCORES (DF=2)	INSHORE/NEARSHORE/ OFFSHORE ZONES KRUSKAL WALLIS SCORES (DF=2)
iron	3.45**	28.75**	30.00**	57.02**
aluminium	3.60**	31.28**	22.87**	53.76**
barium	2.97**	23.06**	14.04**	43.08**
copper	2.41**	4.02	15.99**	16.96**
DO	-	-	19.10**	35.89**
S.S.	3.54**	36.72**	1.80	26.69**
temperature	1.50	13.23**	-	19.75**
conductivity	4.77**	53.86**	27.09**	82.17**
turbidity	5.78**	66.78**	45.48**	104.53**
phosphorus	4.00**	25.03**	38.45**	66.55**
Kjeldahl	4.03**	36.15**	23.10**	58.51**

* significant difference at $P<0.05$
**significant difference at $P<0.01$

To further the investigation of possible zones for water quality characterization, arbitrary zones were created dividing the inshore area into 2 discrete units: north and south of the Kaministikwia River. This pattern takes into account the observation from current meter results that the Thunder Bay area is generally flushed from the north and that pollutants entering the study area are likely carried southward towards the open lake. A separate zone, the offshore zone, was delineated to account for those stations not as greatly affected by nearshore inputs. Results from a Kruskal Wallis test again revealed significant differences among the zones in concentrations of iron, aluminium, barium, copper, dissolved oxygen, conductivity, turbidity, phosphorus and total Kjeldahl nitrogen. In this case, suspended solid results were the exception, that is, any differences among zones were not considered significant.

A final approach used 3 zones, inshore, nearshore, and offshore (Figure 13). Although arbitrary, these zones were created based on the scores from the principal component. The station component scores represent the spatial/temporal relationships of the parameters which were highly correlated with the first component (i.e. turbidity, pH, BOD, conductivity, dissolved oxygen, total Kjeldahl nitrogen, nitrite nitrate, phenols and chloride). The component scores for each survey day are presented in Figures 10 to 12. The general pattern observed over the three day period approaches the three zones chosen for spatial comparisons. The t statistics generated by the Kruskal Wallis analysis were the highest for this pattern, that is, the greatest difference among the zones was observed with this pattern and all of the parameters previously mentioned differed significantly among the zones at the 99 percent confidence interval (Table 9).

It may be concluded from the above analyses that the distribution of conventional parameters, at least, indicates that the zone of most degraded water quality is close to shore and in an area that radiates out from the Kaministikwia River delta. The zone of influence extends as far out as the Welcome Islands. South of this zone of influence, towards Pie Island and the open lake, the physical parameters, nutrients levels and heavy metal concentrations are similar to background conditions.

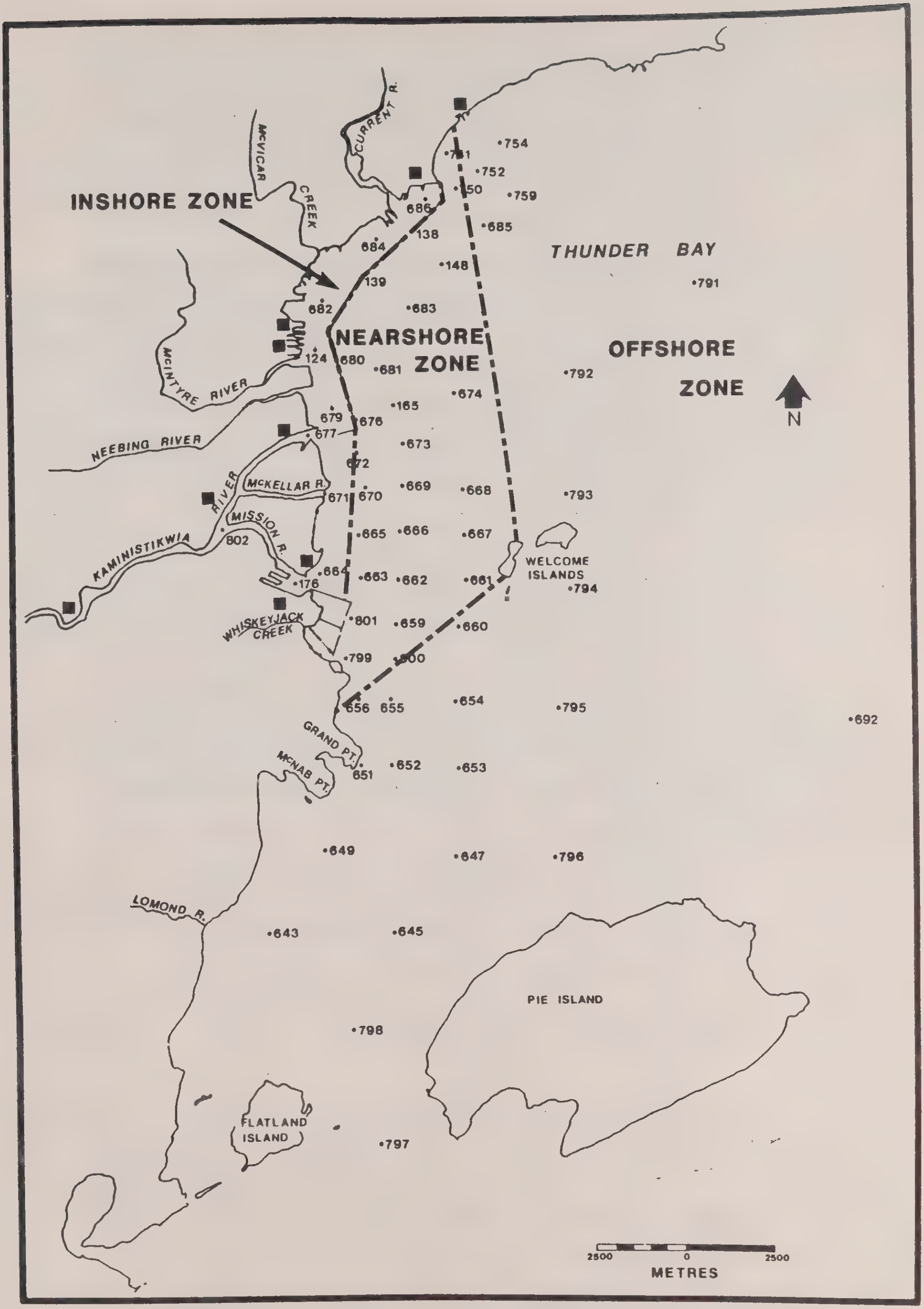


FIGURE 13 : ZONATION PATTERN USED FOR THUNDER BAY COMPARISONS, 1970-1983

Temporal Variation

Day to day differences in the 1983 data were examined using the data from selected parameters (conductivity, turbidity, total phosphorus and iron) collected over the three day survey. These results were expressed as a deviation from the 3-day mean for each station and compared using a Kruskal Wallis test. This removes the station location effects so that only the daily variation in parameter concentrations is observed.

Significant daily differences were found with total phosphorus, conductivity and turbidity (Table 10). Iron concentrations did not differ over the three-day period. Phosphorus levels showed a marked increase on the third day of sampling. Field observations supported a change in conditions on this day including an apparent noticeable change in water temperature. Weather data recorded at the Environment Canada meteorological station in Thunder Bay also show higher winds (average 12.3 Km/hr) from the south-southwest on the third day of sampling.

Because of the daily variability encountered in the 1983 data, conclusions based on a three-day sampling regime are somewhat subjective. Comparisons of seasonal conditions and year to year changes must be carried out with due regard to the fluctuating nature of water quality conditions in nearshore areas. Assessing the degree of variability commonly encountered in an area of study would provide useful information in determining optimal sampling frequency and future sampling needs. Towards these ends three samples over three days for each location in an area as complex as Thunder Bay has been an inadequate approach.

TABLE 10: KRUSKAL WALLIS TEST RESULTS FOR DAILY VARIABILITY IN THUNDER BAY 1983 WATER QUALITY DATA

Parameter	test score	N	Probability
total phosphorus	76.059**	180	-1.000E-13
turbidity	20.540**	93	3.466E-05
conductivity	20.086**	147	4.349E-05
iron	2.742	87	0.2538

* significant difference at P<0.05
**significant difference at P<0.01

A one-day nearshore surveillance survey of nineteen stations in the Thunder Bay area was carried out by MOE on May 18, 1983. Results generated by this survey have been used to make general comparisons with the conditions observed in July. Changes in station locations, sampling depth, sampling intensity, wind and wave conditions are all factors which must be taken into account when making comparisons between seasons.

Seasonal comparisons in Thunder Bay data have been expressed graphically in the form of box plots. This method of presentation shows the following data set information: the median or middle value of an ordered data set, the maximum and minimum points, the 25% and 75% quantiles and relative sample size. Box plots not only show general changes in the data but also the variation and skewness of the results. Seasonal variation in Thunder Bay phosphorus, phenol and dissolved oxygen results have been presented in Figures 14 to 16.

Little change was observed between spring and summer in phosphorus and phenol results. In both examples, the extreme values were measured during the summer survey in the lower Kaministikwia River and delta, an area not included in the spring survey. Seventy-five percent of the phosphorus and the phenol results in both surveys met the Provincial Water Quality Objectives and Guidelines (20 ug/L phosphorus and 1 ug/L total phenols). As expected, dissolved oxygen in Thunder Bay waters decreased in the summer with the majority of the results (greater than 75%) less than the lowest spring observation of 10.4 mg/L. Calmer wind and wave conditions in summer and reduced vertical mixing account for this difference in dissolved oxygen concentrations.

There is a high degree of variation possible in water quality data obtained over a number of years because of changes in survey approaches, detection limits, the analytical techniques employed, and the natural cycles of high or low water years. Comparisons among years therefore, are largely subjective and are best performed in a simple and straight forward manner. Because of the high discrimination exhibited among the arbitrarily created inshore, nearshore and offshore zones previously discussed, this zonation pattern was used in a comparison of data collected by MOE since the 1970 Regional water

FIGURE 14

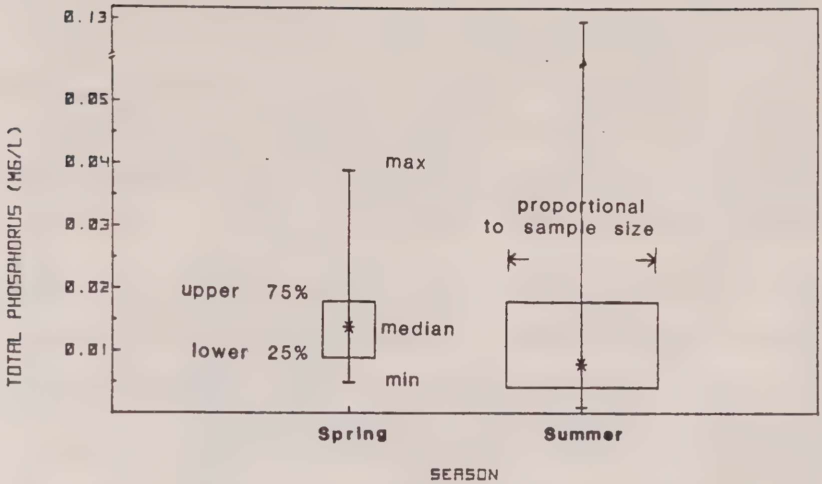


FIGURE 15

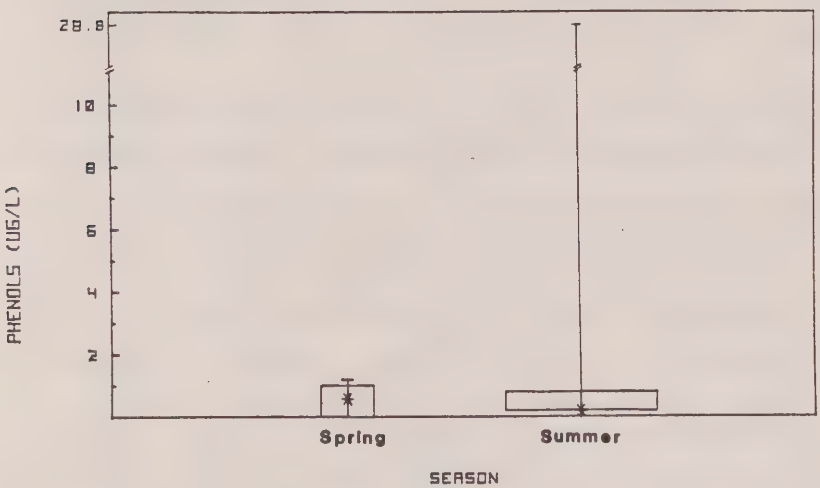


FIGURE 16

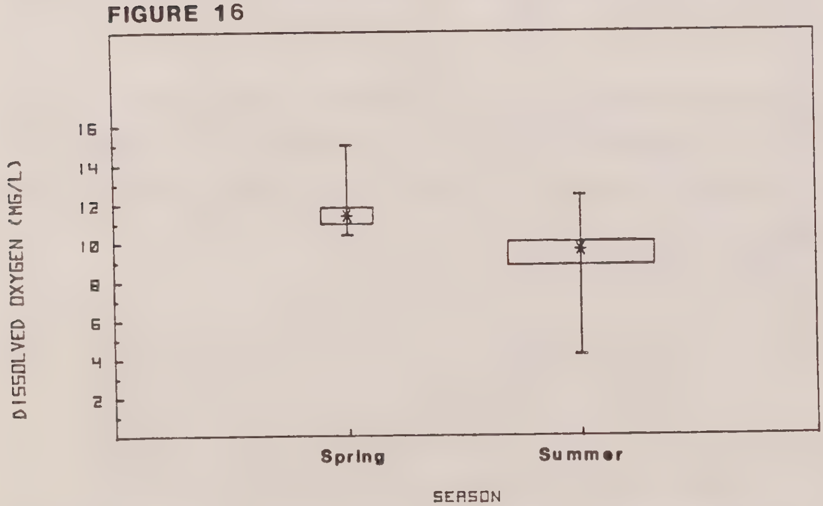


FIGURE 14-16: SEASONAL VARIATION IN TOTAL PHOSPHOROUS , PHENOL AND DISSOLVED OXYGEN CONCENTRATIONS IN THUNDER BAY, 1983

quality survey. Data from the various surveys performed in the Thunder Bay area from 1970 to 1983 have been presented in the form of box plots to illustrate general changes in phosphorus, phenol, dissolved oxygen, iron and copper concentrations (Figures 17 to 21).

As seen in the plots, the ranges of concentrations vary a great deal from year to year; however, the median values and the inner 50% values of the data sets vary to a lesser degree. Phosphorus results in 1977 were extremely variable with a maximum concentration of 0.4 mg/L, although the medians for total phosphorus in the inshore and nearshore areas were 0.019 mg/L and 0.0095 respectively, somewhat lower than other years. Maximum observed levels of total phosphorus in 1979 and 1983 appear to have declined, particularly in the inshore zone.

Total phenol concentrations also appear to have decreased especially when compared with the 1979 data. Although extreme values were evident throughout the waterfront, and particularly in the "nearshore" zone, most of the observations approached or met the Provincial Water Quality Objective for phenols (1.0 ug/L). Dissolved oxygen concentrations fluctuated routinely and the years between 1970 and 1983 have shown no noticeable change. The metals, copper and iron, were compared with 1973 data and a definite decrease overall was observed in 1983. Both iron and copper levels, at most locations approached more closely or met the Objectives for these parameters in 1983 whereas the 1973 levels were consistently in excess of these limits.

Although the arbitrary zones created for comparisons are not statistical or limnological entities, their purpose as a descriptive tool has assisted somewhat in determining the nature and extent of the water quality impairment in Thunder Bay and has provided a worthwhile basis for comparing data from previous years.

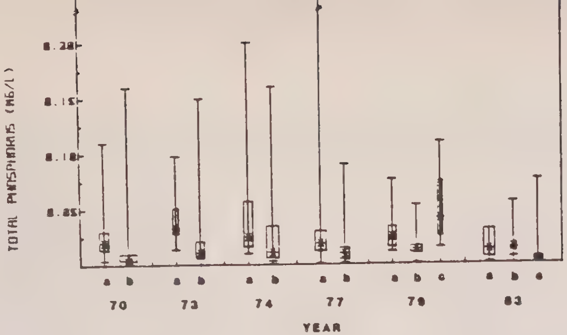


FIGURE 17

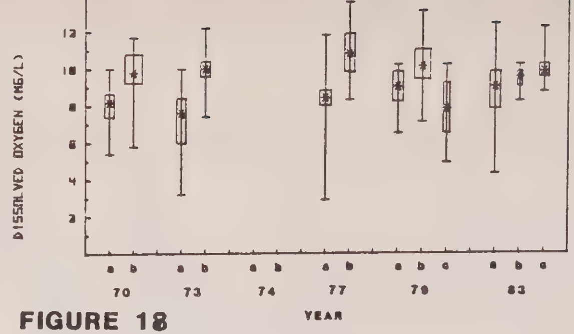
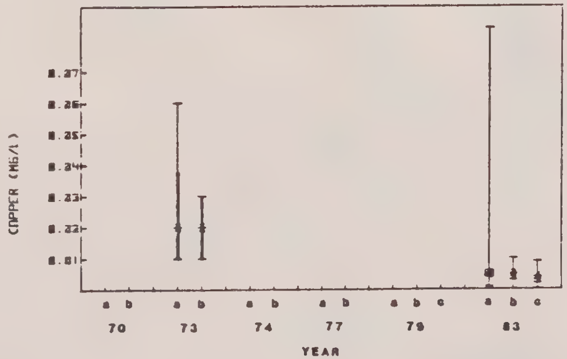


FIGURE 18

FIGURE 19



a - INSHORE ZONE

b - NEARSHORE ZONE

c - OFFSHORE ZONE

FIGURE 20

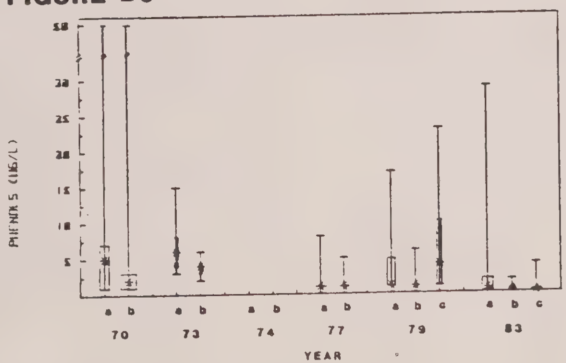


FIGURE 21

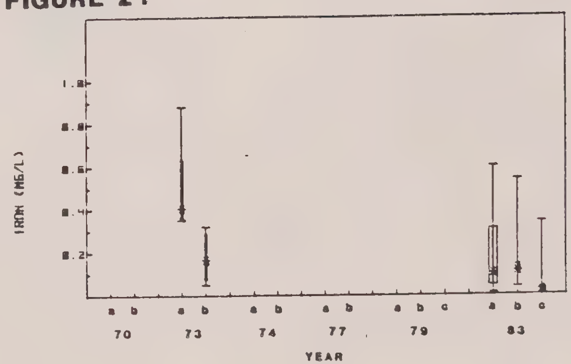


FIGURE 17-21: VARIATION IN THUNDER BAY PHOSPHOROUS, DO, COPPER, PHENOL AND IRON CONCENTRATIONS, 1970-1983

SEDIMENTS

Sediment results from a study conducted by MOE in 1979 appear in Tables 11 to 13. Sediment sampling stations are shown in Figure 22. The 1979 data identified total reactive phenolics and resin, aromatic and fatty acids in Thunder Bay sediments at concentrations as high as 0.30 ug/g for total reactive phenolics and 182 ug/g for total resins in the inner harbour in the vicinity of Provincial Papers Division of Abitibi Price Inc. These compounds are indicative of pulp and paper mill discharges. However, no guidelines presently exist for these compounds in sediments.

Levels of PCB's, heavy metals and nutrients in excess of MOE guidelines necessitate the confined disposal of spoils from many of the areas which are subject to maintenance navigation dredging. Contaminated spoils are placed in a confined disposal facility located south of the Kaministikwia River delta (Figure 2).

In the north end of the Thunder Bay inner harbour, at station 135, the greatest contamination of sediments was found. Of all the stations sampled, station 135 had the highest levels of most metals (copper, lead, mercury, zinc), acids, ether solubles and PCB's. As well, the highest levels of pp DDE, gamma BHC (Lindane), phenols, total Kjeldahl nitrogen and total carbon were observed at this location. A lagoon discharge for Abitibi-Price Provincial Papers Division is located at the northern-most end of the harbour at Bare Point near to sampling station 135. Water quality results from 1983 indicate elevated levels of total phosphorus and turbidity in this area, however, levels of other parameters which were high in 1979 sediments were found to be low or not detected in 1983 water samples.

At the mouth of the McKellar River (Station 671) levels of tannins, lignins, and some aromatic acids were the highest found in the study area. As well, neoabietic acid, dieldrin and sulphur concentrations were elevated when compared to other locations. All sediment stations sampled had detectable levels of PCB's and ppDDE with the exception of Station 690 on the Kaministikwia River.

Mercury concentrations when compared to 1971 survey results have shown a dramatic decrease from a 1971 maximum of 27 mg/kg and average value of 2.97 mg/kg to a 1.5 mg/kg maximum and 0.32 mg/kg average in 1979. The maximum levels observed in both surveys were in sediments obtained from the northern end of the inner harbour.

FIGURE 22: SEDIMENT SAMPLING LOCATIONS, 1979 SURVEY

TABLE 11. SUMMARY OF 1979 THUNDER BAY SEDIMENT SURVEY RESULTS FOR HEAVY METALS (ug/g) NUTRIENTS (mg/g) AND PARTICLE SIZE

Parameter	Station										
	135	519	521	542	553	677	176	671	690	691	692
cadmium	0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	0.7	<0.4
chromium	45	75	31	27	44	33	38	48	25	54	61
copper	79	37	26	16	36	27	41	57	12	56	59
lead	67	6	5	5.8	6.5	6.2	3	8	<3	18	19
mercury	1.5	0.03	0.15	0.12	0.24	0.14	0.17	0.28	0.04	0.43	0.37
nickel	31	40	20	17	31	22	26	35	15	35	39
zinc	170	91	68	79	87	83	100	140	70	140	130
total phosphorus	0.65	0.61	0.63	0.44	0.51	0.61	0.61	0.85	0.40	1.2	0.82
total Kjeldahl nitrogen	2.8	0.56	0.59	0.51	0.50	0.66	0.63	1.5	0.29	1.8	1.4
total carbon	99	23	10	6.5	11	12	14	22	5.8	22	17
total organic carbon	-	-	-	-	-	-	-	-	-	21	14
total sulphur	2.1	0.2	0.4	0.1	0.2	0.4	0.8	2.4	0.1	0.54	0.39
particle size:											
% gravel	mainly	0	0	0	1.0	1.2	0	0	3.3	0.3	0.3
% sand	paper	1.8	51.6	65.6	27.5	52.6	13.9	17.7	91.4	7.2	8.5
% silt		11.7	36.7	28.4	41.0	34.0	58.1	52.1	2.4	43.3	32.6
% clay		86.5	11.5	6.1	30.5	12.2	28.0	30.2	2.9	49.2	58.6
pH (field)	-	7.78	6.98	6.98	6.58	7.08	7.22	7.12	-	-	-

TABLE 12. SUMMARY OF 1979 THUNDER BAY SEDIMENT SURVEY RESULTS FOR TANNIS, LIGNINS, RESIN ACIDS, FATTY ACIDS, AROMATIC ACIDS AND ETHER SOLUBLES (mg/kg).

Parameter	Station											Detection Limit
	135	519	521	542	553	677	187	671	690	691	692	
tannins	125	13	25	31	25	25	12	375	31	31	-	0.5
lignins*	312.5	32.5	62.5	77.5	62.5	62.5	30	937.5	77.5	77.5	-	-
Resin Acids												
pimaric	24	ND	1	4	1	2	3	21	0.110	1	0.7	0.010
sandaracopimaric	20	ND	2	4	0.8	0.6	1	8	ND	0.8	0.5	0.010
levopimaric	12	ND	2	ND	ND	0.4	ND	Trace	ND	ND	0.2	0.010
isopimaric	14	ND	0.3	1	0.6	0.3	0.3	2	0.010	2	0.7	0.010
neoabietic	ND	ND	ND	1	ND	ND	ND	2	ND	0.9	0.4	0.020
abietic	106	ND	2	14	6	4	18	46	0.139	6	2	0.020
dehydroabietic	6	ND	0.3	1	0.4	3	0.9	3	ND	0.5	0.2	0.020
total:	182	ND	7.6	25	8.8	10.3	23.2	82	0.259	11	5	-
Fatty Acids												
capric	0.7	ND	ND	0.1	ND	0.03	ND	0.1	0.003	0.06	0.04	0.005
lauric	1	0.02	0.2	0.1	0.1	0.1	0.1	0.2	ND	0.2	0.1	0.005
myristic	2	0.04	0.3	0.3	0.1	0.2	0.1	0.5	0.038	0.4	0.3	0.005
palmitic	2	0.1	0.3	0.3	0.1	0.1	0.1	0.5	0.051	0.5	0.2	0.005
stearic	0.7	0.1	0.21	P.sep.	ND	0.1	0.1	0.2	0.012	0.1	0.08	0.005
oleic	1	0.1	ND	P.sep.	P.sep.	ND	0.3	0.3	0.017	0.2	0.1	0.005
linoleic	2	ND	0.06	0.1	ND	0.1	0.1	0.4	0.013	0.1	0.08	0.005
linolenic	0.5	ND	0.06	0.1	0.1	0.04	0.1	0.08	0.008	0.1	0.07	0.005
arachidic	1	ND	0.1	0.4	0.2	0.1	ND	0.7	0.021	ND	ND	0.005
total	10.9	0.4	1.2	1.1	0.6	1.1	0.6	3	0.163	1.0	1.0	-
Aromatic Acids												
benzoic	0.7	ND	0.1	0.1	0.1	Trace	0.2	0.4	0.015	ND	ND	0.005
salicylic	1	ND	1	0.4	0.5	1	2	5	ND	ND	ND	0.005
phthalic	0.5	ND	0.5	0.2	0.1	0.2	0.3	1	0.020	0.3	0.2	0.005
total	2.2	ND	1.6	0.7	0.7	1.2	2.5	6.4	0.035	0.3	0.2	-
ether solubles	1,461	86	366	195	237	370	230	1,021	108	566	741	1.0

ND. = Not detected   a dash (-) indicates no data available   * = 2.5 times Tannins value
P.Sep. = Poor separation in gas chromatograph.

TABLE 13: SUMMARY OF 1979 THUNDER BAY SEDIMENT SURVEY RESULTS FOR PCB's, TRACE ORGANICS AND TOTAL PHENOLS (ug/g).

Parameter	Station											Detection Limit
	135	519	521	542	553	677	176	671	690	691	692	
PCBs	600	220	74	170	140	190	60	120	ND	68	125	10
aldrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1
dieldrin	ND	ND	ND	ND	ND	ND	ND	4	1	ND	ND	1
α-BHC	ND	1	1	2	ND	ND	ND	ND	ND	ND	ND	1
β-BHC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1
Lindane (γ-BHC)	3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1
α-Chlordane	ND	1	3	1	ND	ND	ND	ND	ND	ND	ND	1
γ-Chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1
op-DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5
pp-DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5
pp-DDD	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5
pp-DDE	39	5	4	5	8	9	3	2	ND	5	6	1
DDT + metabolites	39	5	4	5	8	9	3	2	ND	5	6	-
endrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1
HCB	ND	2	ND	ND	1	ND	ND	ND	ND	ND	ND	1
heptachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1
heptachlor epoxide	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1
mirex	ND	ND	2	ND	ND	ND	ND	ND	ND	ND	ND	5
endosulphan I	ND	ND	ND	ND	ND	2	ND	ND	1	ND	ND	1
endosulhan II	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1
total phenols	300	38	50	37	75	63	38	63	50	140	50	1

ND = not detected

BIOTA

Yearling yellow perch and young-of-the-year spottail shiners collected in 1979 contained low levels of PCB's (0.021-0.067 ug/g, whole fish) and total DDT (non-detected - 0.012 ug/g, whole fish). Mirex and HCB were not detected in any of the fish. Mercury levels in fish from Mission Island were 0.05 ug/g whole fish, well below the Great Lakes Water Quality Agreement Objective level of 0.5 ug/g (IJC, 1978).

In 1983, spottail shiners collected in the Mission River were found to contain PCB residues in excess of the IJC Aquatic Life Objective of 100 ng/g (Great Lakes Water Quality Agreement, 1978). Although PCB residue levels in Lake Superior spottail shiners were relatively low compared to levels found in the lower Great Lakes, residue accumulations were found to be significantly higher at Thunder Bay in 1983 when compared to 1979 results (Suns, 1984). DDT and metabolite residues were found to be below the 1 ug/g Objective in the Mission and the Kaministikwia Rivers but have only shown a decline since 1979 in the Mission River collections. Chlordane was detected in both the Mission and the Kaministikwia Rivers in 1979 and was not detected in 1983. BHC residues were non-detectable or near their detection limits. Residues for mirex, heptachlor, aldrin, octachlorostyrene, hexachlorobutadiene, hexachloroethane, trichlorotoluene, as well as chlorobenzene and chlorophenols were non-detectable in all 1983 collections (Suns, 1984).

Some sport fish of all species collected from the Thunder Bay area were considered suitable for unrestricted consumption. In 1979 walleye and white suckers larger than 45 cm in length were found to contain mercury levels in the range of 0.5 to 1.0 ppm and were considered suitable for limited consumption based on the guidelines set forth in the "Guide to Eating Ontario Sport Fish" (MOE/MNR, 1985). Northern pike and lake trout up to 55 cm in length were considered suitable for unrestricted consumption. Lake trout larger than 65 cm in length were further restricted because PCB levels exceeded the 2.0 ppm guideline for this substance.

While the residual effects of chlor-alkali plant mercury inputs may be contributing to the mercury content in the larger fish, the concentrations observed were generally typical of levels found in other fish of the same species from other parts of the lake remote from industrial sources. PCB levels higher than 2.0 ppm in the largest lake trout are typical of levels measured in the larger lake trout from other areas in Lake Superior (MOE/MNR, 1985).

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